

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:

Materials Chemistry and Biomolecular Materials: 1. Electronic Stabilization in Metal-Rich Solid-State Phases

FWP Number: AL-90-360-001

Program Scope: The program seeks to expand our knowledge and understanding of solid-state chemistry by combining experiment—particularly exploratory synthesis and structure—with theory in order to both uncover new families of intermetallic phases and to understand the factors that stabilize both new and known phases. These families include Zintl, cluster, intermetallic, quasicrystalline, and related phases. Experiments encompass high temperature synthesis (arc melting, reactive metal fluxes, sealed metal container) and variable-temperature single crystal and powder diffraction. Theoretical efforts span first-principles to semi-empirical calculations.

Major Program Achievements (over duration of support):

We have explored, developed and organized a new field of polar intermetallics formed between active metals and the triels (Ga, In, Tl), discovering much unique chemistry beyond the classical Zintl (valence) boundary. We synthesized and characterized new Zintl (valence) and related compounds: $K_{39}In_{80}$, K_5InPb_8 , a Bergman-type structure in $Na_{11}(Cd,Tl)_{27}$, tetrahedral stars in K_6Tl_{17} , and new hyper-electronic networks ($SrIn_4$, Sr_3In_5) with relatively low numbers of cations. We identified and interpreted electronic deviations from Zintl concepts in terms of structure, properties, and theory, for example, electronic tuning via Li, Mg substitutions in triel networks, and the importance of atom size limitations in the stability of certain classical structure types. New e-poorer intermetallic phases exhibiting important relativistic effects were defined for the substituted triel phases Ba_2AuTl_7 , Sr_2PtTl_2 , $BaAuIn_3$, and $BaHgIn$. Five problem cases have been studied by ab-initio methods, demonstrating the absence of the closed shell (Zintl) anions Pb^{-4} , Bi^{-3} and Ge_2^{-6} in certain salts and the major role of sodium in the bonding in Na_3AuIn_2 , Na_6TlSb_4 and KNa_3In_9 . We have refined a new series of binary Hume-Rothery-type intermetallics in the Zn-Pd system that provide greater insights into the stability of cubic gamma-brass structures, their relationships to quasicrystals, and some general aspects of the influence of electronic structure on complex intergrowth structures. $Zn_{1-x}Pd_x$ ($0.15 \leq x \leq 0.25$) have been prepared (see also Bulk Structures) with six structures identified. Electronic structures show pseudogaps at the corresponding Fermi levels, with these features driven by Zn-Pd and Zn-Zn orbital interactions. We also observe specific site preferences for Pd at the center of Zn-rich icosahedra, and this can be understood from theoretical calculations as well.

Program Impact:

Our discoveries have impacted or motivated solid-state chemistry concepts and programs around the world and have correspondingly attracted students and visitors from many places. This impact includes groups utilizing a combination of experiment and theory to investigate problems in solid-state chemistry, as well as to pursue thorough characterization of products beyond crystal structure determinations.

Interactions (External):

PNNL; U.S. Universities at Notre Dame, Houston, Northwestern, Michigan State, Utah State, Arizona State. Overseas organizations: Max-Planck Institutes at Stuttgart & Dresden; LGChem, Korea; FJIRSM, Fuzhou, China. Foreign Universities at Barcelona (Spain), Aachen, Cologne, Muenster & Munich (Germany), and Stockholm (Sweden).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Co-organizers, Symp. on The Chemistry of Intermetallics and Zintl Phases at 226th ACS meeting (JDC & GJM '03); National Academy of Sciences (JDC '92); two ACS National Awards in Inorganic Chemistry (JDC '86 & '00); 2 DOE Awards in Materials Chemistry (JDC '87 & '95); F. H. Spedding Award (JDC '05); Visiting Professor, ETH-Zürich (GJM '00). Total of 19 invited talks and 29 refereed papers in this subtask since 2002.

Personnel Commitments for FY2005 (Actual Effort):

J. Corbett (40%); G. Miller (5%); B. Li (100%); J. Dai (100%); S. Standley (20%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$253,000

FY04 BA \$265,000

FY05 BA \$260,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or subtask Title under FWP:

Materials Chemistry and Biomolecular Materials: 2. Bulk Structure and Structure-Property Relationships in Intermetallics and Metal-Rich Solid-State Inorganic Compounds.

FWP Number: AL-90-360-001

Program Scope: The goal is to elucidate the atomic positions in complex solid-state materials, and in some cases to understand how this structure relates to physical properties, such as thermoelectric or magnetocaloric properties.

Major Program Achievements (over duration of support): (1) Toward quasiperiodicity in one-dimension: Exploration of the $\text{Zn}_{1-x}\text{Pd}_x$ binary system ($0.15 \leq x \leq 0.25$) identified a series of structures with unit cells showing two sides with common lengths and the third varying greatly, some with distances in excess of 100 Å. We were successful to interpret these structures as intergrowths based on two different icosahedral blocks, and have developed an “algorithmic” method to prepare new structures that may lead to a one-dimensional quasiperiodic system. Two structures were solved using super-space group methods. Electron diffraction studies also show superstructures. These structures are related to the Hume-Rothery gamma-brasses, and similar behavior occurs in $\text{Mn}_{1+\delta}\text{Ga}_{1-\delta}$. (See also Electronic Stabilization) (2) Crystalline CrGa, MnGa, FeGa and the new compounds $\text{Cr}_x\text{Fe}_{1-x}\text{Ga}$ ($0 < x < 1$) were identified, structurally characterized by X-ray and neutron diffraction, and studied for their magnetic properties. This isostructural series is a set of approximants for icosahedral quasicrystals rich in transition metals. There is a change from antiferromagnetic to ferromagnetic behavior along the binary sequence, while Cr and Fe order according to local magnetic exchange seen in “MnGa.” $\text{Mn}_{1+\delta}\text{Ga}_{1-\delta}$ shows formation of the cubic gamma-brass type. (3) Phase Changes in “ Zn_4Sb_3 .” “ Zn_4Sb_3 ” is, in fact, $\text{Zn}_{13}\text{Sb}_{10}$, which undergoes a solid-solid phase transition at 767 K and then decomposes into ZnSb and Sb before reaching its “melting temperature” of 841 K. The structure of $\text{Zn}_{13}\text{Sb}_{10}$ is characterized by disorder at many Zn sites and show two distinct phase transitions below room temperature. Complete characterization of its temperature-dependent physical properties corroborate the structural characterization. (4) Technique Development. A technique for performing high-temperature, single crystal X-ray diffraction of air-sensitive compounds was developed in the past year and applied to study the high-temperature phase changes in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and related phases. The technique involves using silica capillaries with inserted silica rods and creating a small volume for a “getter.” This area, which contains metal powder that reacts with oxygen and/or nitrogen at elevated temperatures, is heated before high-temperature XRD experiments are run on the single crystal specimen. Using this technique we have numerous problems in magnetic refrigeration materials, $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ and $\text{Gd}_5(\text{Ga}_x\text{Ge}_{1-x})_4$; (5) Structure and composition analysis of complex intermetallics: $\text{RT}_2\text{Zn}_{20}$ ($T = \text{Fe, Co}$; $R = \text{rare-earth element}$) show complex icosahedral networks. We have combined X-ray and neutron diffraction to elucidate the distribution of T and Zn atoms. There is also some unusual thermal behavior of the R site, which sits in a large coordination polyhedron (similar to large thermoelectric materials, skutterudites), and we continue to explore these structures (in collaboration with P. Canfield).

Program impact: This research continues a strong tradition within the Materials Chemistry Program at the Ames Laboratory of the discovery of new phases, and the delineation of their structure, as well as their structural variation with temperature and with conditions of formation.

Interactions (External):

APS at Argonne, Los Alamos; Stanford. Overseas organizations: Max-Planck Institutes at Dresden; Foreign Universities at Aachen & Munich (Germany), and Stockholm (Sweden).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Visiting Professor, ETH-Zürich (GJM ‘00); Co-Organizer, Symp. on The Chemistry of Intermetallics and Zintl Phases at 226th ACS meeting in New York City (GJM ‘03); Symp. Co-Organizer, Quasicrystals, MRS Fall Meeting (DJS ‘03); Conference Co-Organizer, 9th International Conference on Quasicrystals, Ames (DJS ‘05); Member of International Program Committee for 12th LAM Conference (DJS ‘04). Total of 7 invited talks & 6 refereed papers in this topic area since 2002.

Personnel Commitments for FY2005 (Actual Effort):

G. Miller (30%); D. Shechtman (40%); M. Besser (20%); X.-F. Guo (100%); H. Ko (25%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$85,000

FY04 BA \$125,000

FY05 BA \$130,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:

Materials Chemistry and Biomolecular Materials: 3. Surface Structure and Structure-Property Relationships in Metal-Rich Solid-State Phases

FWP Number: AL-90-360-001

Program Scope: The goal is to elucidate intrinsic structural and functional aspects of complex intermetallics, with particular attention to the structure-property relationships. The structural and functional aspects include atomic positions, electronic structure, friction, and chemical reactivity.

Major Program Achievements (over the last 3 years): (1) Atomic and Electronic Structure: Our work is at the forefront of understanding the nature of the clean surfaces of quasicrystals. We use various ultrahigh vacuum surface-sensitive techniques including scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy, and angle-resolved low-energy ion scattering (LEIS) to probe these surfaces. We recently discovered that the steps of these complex materials are naturally rougher than their crystalline counterparts. In collaboration with J.-Y. Park and M. Salmeron from LBNL we have been able to directly measure, using atomic force microscopy (AFM), the fields produced by step dipoles. We also showed that temperature effects play a vital role in surface structure. A temperature change from 900 to 925 K is sufficient to dramatically alter the quasicrystal terraces; at the lower temperature, a distinctive void-rich termination is common. These results provided a new insight into the way that a surface evolves toward the quasicrystalline structure. (2) Reactivity: By probing the interaction of hydrogen with Al-Pd-Mn using LEIS, we showed that, unlike molecular hydrogen, atomic hydrogen readily adsorbs at specific types of sites on the surface. (3) Interfacial Growth: We obtained evidence of quantum size effects in growth of Ag on a quasicrystal surface, which leads the film to grow as flat-topped mounds with preferred heights. This is ascribed to the electronic pseudogap of the bulk quasicrystal, and the fact that it is present up to the surface of the quasicrystal. We had previously established its presence at the surface by using x-ray photoelectron spectroscopy. (4) Friction and Wear: With M. Salmeron and J.-Y. Park, we used AFM to examine the fundamental role of periodicity in friction. Our results demonstrate an 8-fold anisotropy in the friction force on a twofold surface of decagonal Al-Ni-Co. (The atoms are aperiodically spaced along one direction of this surface and periodically along the other.) The highest friction force was measured in the periodic direction, the lowest in the aperiodic direction, hence demonstrating that low friction forces are intrinsic to the aperiodic arrangement. This work was published in *Science* in 2005. (5) Conference Organization: In 2005, C. Jenks, D. Sordélet and P. Thiel co-organized the 9th International Conference on Quasicrystals. Over 180 people from 21 different countries attended. The conference proceedings will be published in early 2006 in Philosophical Magazine. Additional information is available online at <http://www.icq9.ameslab.gov>.

Program Impact: Our work to date has culminated in the acceptance in the field that atomically flat quasicrystalline surfaces can be produced and that these surfaces are laterally bulk terminated; this work has implications for the relative importance of three-dimensional clusters in stabilizing the icosahedral structure. It has also demonstrated that low friction is intrinsic to the aperiodic atomic structure of a clean quasicrystalline surface, laying to rest the possibility that low friction in these materials is due (solely) to hardness or oxide chemistries, as had been previously speculated. In addition, our work has motivated and facilitated many new research projects around the world.

Interactions (External):

U.S. Natl. Laboratories: ANL, LBNL, SNL. U.S. Institution: Carnegie Mellon Univ., Penn. State Univ. Foreign Institutions: Dalian Univ., ETH-Zürich, NIMS (Japan), CNRS-Nancy, Institut für Festkörperforschung Jülich, Univ. Liverpool, Univ. Magdeburg, Univ. Newcastle.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Co-Organizers, 9th Intl. Conf. on Quasicrystals (CJJ & PAT '05); Dr. Honoris Causa (honorary degree) from the Institut National Polytechnic de Lorraine (PAT '05), Distinguished Professor of ISU (PAT '02); Fellow of the AVS (PAT '01); Fellow of the APS (PAT '01); ISU College of Liberal Arts and Sciences Award for Professional & Scientific Staff Excellence (CJJ '99); DOE Award for Outstanding Scientific Accomplishment in Materials Chemistry (CJJ & PAT '98). Total of 29 invited talks and 30 refereed publications in this topic area from FY03 – FY05.

Personnel Commitments for FY2005 (Actual Effort):

C.J. Jenks (70%); J.Y. Park (10%); P.A. Thiel (40%); B. Unal (50%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$339,000

FY04 BA \$380,000

FY05 BA \$380,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:

Materials Chemistry and Biomolecular Materials: 4. Solute Effects in Metal-Rich Solid-State Phases

FWP Number: AL-90-360-001

Program Scope: The goal is to combine experiments and theoretical calculations to elucidate the effect of small concentrations of atomic solutes on phase stability, formation pathways, and high-temperature phase transitions in solid-state inorganic materials. Control of low levels of solutes can be very difficult, but this is often possible for groups within the Ames Laboratory because of the specialized synthesis and novel characterization expertise and facilities developed here.

Major Program Achievements (over the duration of support):

When the eutectic composition of $Zr_{80}Pt_{20}$ is quenched rapidly, the literature reports that an amorphous structure forms, perhaps along with a fraction of a metastable icosahedral (quasicrystalline) phase. Using special techniques to reduce O solute contents, we discovered that a bcc β -Zr(Pt) phase is formed, which is in complete contrast to the universal assumption that reducing O content increases the glass forming ability in metallic liquids. A structural model comprised of a $3 \times 3 \times 3$ stacking of the primitive bcc β -Zr structure with Pt atoms to define superlattice positions was shown using *ab initio* calculations to be energetically favorable over other structures. In addition, experiments show that a transition to an Fd3m (Ti_2Ni -type) Zr_6Pt_3O structure (i.e., the 'big cube' phase) occurs as the O level increases. This structure contains clusters having local icosahedral order. The experimentally observed transition from β -Zr(Pt) to quasicrystalline to 'big cube' metastable phases with increasing O contents has been further supported by first-principles calculations using approximate Zr:Pt stoichiometries and O solute atom concentrations. Recently, studies of O content on phase selection during crystallization of off-eutectic amorphous Zr-Pt alloys (e.g., $Zr_{71}Pt_{29}$ - $Zr_{78}Pt_{22}$) have shown that the stable Zr_5Pt_3 and 'big cube' Zr_6Pt_3O phases are in competition and influence the energy landscape leading towards selection of metastable or equilibrium crystallization phases.

Among the Zintl-related polar intermetallics, we have found numerous phases that are stabilized by hydrogen or other small interstitials, especially those of the tetrels (Si-Pb) and triels (Ga-Tl) with alkaline-earth metal counterions. Many examples have Mn_5Si_3 -type structures. Recent examples include Sr_5Ti_3 , La_3In_{11} , and Yb_5Sn_4 , all of which are actually hydrides. Many polyanionic clusters of Ga, In and Tl have been found that also take up transition metal atoms as interstitials in stoichiometric amounts, e.g., $Rb_8Tl_{11}Pd$, whereas small amounts in other clusters allow the alteration of electron counts and, therewith, stabilities.

Program Impact:

A common result is the discovery that phases reported previously in the literature were, in fact, solute-stabilized and exist only as such. It is extremely important to correct such mistakes for many reasons, among them the fact that reliable experimental data is necessary to validate high-level theory for complex solid-state systems. This is also true for metastable phases such as in the Zr-Pt system, which may well lead to a deeper understanding of the relationship between quasicrystalline and crystalline systems, in particular how bonding and local coordination evolve in a seemingly continuous manner between aperiodic and periodic structures.

Interactions (External):

Advanced Photon Source at ANL; INEL; LANL; ORNL; PNNL. US Universities at Notre Dame, Houston, Northwestern, Michigan State, Utah State, Arizona State. National Laboratories and Industries Overseas, at CNRS--Nancy (France), Max-Planck Institutes at Stuttgart and Dresden (Germany), LGChem (Korea), FJIRSM, Fuzhou (China). Foreign Universities at Barcelona (Spain), Cologne, Munich, Darmstadt, Karlsruhe (Germany).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Plenary Lecturer at Intl. Symp. on Metal Hydrides (JDC '02); F. H. Spedding Award in Rare Earth Research (JDC '05); Symp. Co-Organizer, Quasicrystals, MRS Fall Meeting (DJS '03); Conf. Co-Organizer, 9th Intl. Conf. on Quasicrystals, Ames (DJS '05); Member of Intl. Program Comm. For 12th LAM Conf. and Intl. Adv. Comm. for the Intl. Conf. on Solidification Sci. & Process. (DJS '04). Total of 15 invited talks and 36 refereed papers since 2002.

Personnel Commitments for FY05 (Actual Effort):

D. Sordelet (50%); J. Corbett (20%); M. Kramer (10%); M. Besser (40%)

Authorized Budget (BA) for FY03, FY04 and FY05

FY03 BA \$354,000

FY04 BA \$300,000

FY05 BA \$280,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:

Materials Chemistry and Biomolecular Materials: 5. Macroscopic Growth of Metal-Rich Solid-State Phases

FWP Number: AL-90-360-001

Program Scope: A first goal is to design, discover, grow, and characterize novel materials with exotic and/or interesting physical properties. A second goal is to stimulate the international scientific community by sharing our high-quality samples in collaborative studies. Emphasis is placed on quasicrystalline and large-unit-cell crystalline materials. The size and quality of our samples allows the measurement of intrinsic material properties, circumventing the (oft-critical) relationship between growth quality and properties that can lead to spurious results.

Major Program Achievements (over last three years): Over the past three fiscal years this program has studied a variety of quasicrystalline and related systems, particularly ones that can be grown in high quality, single grain form via high temperature, metallic solution growth and via Bridgman growth. Following the report of the first thermodynamically stable binary quasicrystalline phases by A.P. Tsai in 2000, we are the only group that has been able to develop synthesis routes leading to large (up to 2.5 cm³) single grains of these phases, specifically the Cd–Yb icosahedral phase (Cd₈₄Yb₁₆), its hexagonal approximant (Cd₅₁Yb₁₄) and the cubic approximant (Cd₈₆Yb₁₄). Thus, the research group was able to study the correlations between local and long-range order in the quasicrystal phase and its corresponding approximant phase. High resolution transmission electron microscopy (HRTEM) and image simulation techniques through focal images revealed a high degree of structural perfection and the remarkable similarity between the local atomic structure of the QC and its approximant phase. This program also made single crystals of icosahedral phase (Cd₁₇Ca₃) and cubic approximant phase (Cd₆Ca). The characterization by HRTEM on these compounds is ongoing. In addition, this group is the first one to grow centimeter-sized Zn-Sc single grain approximant phase which are sufficient for neutron scattering studies. Synthesis of Zn-Sc-Mg single grain quasicrystal is in progress. According to the prediction by M. Mihalkovic (2004) of aperiodic compounds in Mg-Ru-B, we have developed processing techniques to grow single crystals of Mg-Ru-B. Characterizations by powder XRD and single crystal diffraction showed that these single crystals do not correspond to the two known approximant phases. Further structure determination is ongoing. Continued development of new synthesis methods focused on combining different techniques is ongoing.

Program Impact: The international impact of this program has been tremendous. We taught the world-wide quasicrystal community how to grow single grain quasicrystals from metallic solutions. The growth techniques developed in Ames Laboratory are now used by many of the other groups throughout the world to make high quality single grains of these compounds. Another achievement has been the sharing of samples for collaborative research. Over 30 labs throughout the world have used the high quality quasicrystals samples synthesized at Ames Laboratory, thus allowing the field to advance at a pace faster than otherwise possible. Through such collaborations, for example, our samples have led to consensus on the fundamental surface structure of icosahedral quasicrystals.

Interactions (External): U.S. National Laboratories: ANL, BNL, LBNL, LANL, SNL; U.S. Universities at Carnegie Mellon, Penn. State, Rensselaer Polytechnic, Stanford.; National Laboratories Overseas at CNRS, INPG, ESRF, CEA, ILL, ETH-Zürich, NIMS; Foreign Universities at Banaras, Dalian, Fribourg, Liverpool, Newcastle, Nijmegen, Ottawa, Tübingen.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):

MRS Fall 2003 Best Poster Award (TAL '03); DOE Award for Outstanding Scientific Accomplishment in Materials Chemistry (TAL & CJJ '98); Fellow of the American Physical Society (PCC '02); Divisional Associate Editor for Phys. Rev. Lett. (PCC '02). Total of 57 refereed publications in this topic area since 2002. Note: CJJ awards listed under subtask 3.

Personnel Commitments for FY2005 (Actual Effort):

T. Lograsso (10%); P. Canfield (10%); C. Jenks (20%); D. Wu (50%)

Authorized Budget (BA) for FY03, FY04, FY2005:

FY03 BA \$113,444

FY04 BA \$165,000

FY05 BA \$165,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:

Materials Chemistry and Biomolecular Materials: 6. Bioinspired Polymers: Self-assembling Hydroxyapatite-Organic Nanocomposites

FWP Number: AL-90-360-001

Program Scope: Synthesis and characterization of novel bioinspired polymeric materials that mimic living systems in their abilities to switch among several states in response to the environment and self-assemble hierarchically. Use of these polymers as directed templates for biomineralization processes, to facilitate a bottom-up approach to materials design. Understanding guiding mechanisms of assembly across multiple length scales through combination of experiment and theory. Advanced solid-state NMR techniques for investigating interactions of the polymeric materials with inorganic components and biomolecules.

Major Program Achievements (over duration of support): We have designed and synthesized novel bioinspired pH and temperature-sensitive block copolymers with various cationic blocks that exhibit hierarchical self-assembly from nanoscale micelles to macroscale gels and solids. Small angle neutron scattering and cryo-transmission electron microscopy studies of these polymers in solution indicate a switch from spherical to cylindrical or thread-like micelles upon increasing temperature and pH. These self-assembly processes and spherical to cylindrical transitions were also predicted by molecular dynamics simulations, where the effect of changes in temperature and pH were modeled by changing the relative hydrophobicities of the different blocks in the multiblock copolymer chains. Small angle X-ray scattering studies show that the self-assembled solids exhibit a hexagonal structure formed by the assembly of the cylindrical micelles, which is distinct from the lamellar structure seen in the melt. Since the order in these copolymers actually increases when they assemble in solution as opposed to the melt, these copolymers are ideal templates for mineralization. Different calcium phosphate phases, either hydroxyapatite or brushite, were formed on these micelles in solution based on the conditions used in the templating process, as seen by transmission electron microscopy. Since the self-assembly process is driven by the relative hydrophobicities of the different polymer blocks, these nanoscale micelles coated with thin inorganic shells exhibited self-assembly into gels and solids, just as in the case of the pure polymer. New advanced solid-state NMR techniques were developed to investigate the hybrid organic-inorganic structures formed by self-assembly. These NMR techniques enable measurement of the thickness of the inorganic layer formed as well as compositional information about the inorganic layer at the organic-inorganic interface, which is very difficult to obtain using other established techniques.

Program Impact:

Our research has generated a new class of bioinspired polymers that can reversibly self-assemble into macroscale solids in solution. Self-assembly across multiple length scales is key to development of a "bottom-up" approach to materials design and the ongoing work will enable the development of novel hybrid organic/inorganic materials formed by hierarchical self-assembly. We have developed NMR techniques that are being used worldwide by other groups.

Interactions:

Argonne National Laboratory; Univ. of Paris, EPFL; Technion, Israel; Koc University, Turkey.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

NSF-CAREER award (SKM, '00); ISU Early Excellence in Research award (SKM, '01); MIT's Technology Review's "Top 100 Young Innovators" list (SKM, '02); John H. Dillon Medal of the American Physical Society (KSR-'01). 14 refereed publications and 16 invited talks since 2002.

Personnel Commitments for FY2005 (Actual Effort):

S.K. Mallapragada (20%); M. Determan (50%); A. Agarwal (50%); A. Travesset-Casas (10%); J. Anderson (5%); K. Schmidt-Rohr (5%); A. Rawal (5%); M.A. Akinc (10%); X. Wei (50%); D. Enlow (50%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$208,000

FY04 BA \$245,000

FY05 BA \$245,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or subtask Title under FWP:

Materials Chemistry and Biomolecular Materials: 7. NMR Technique Development

FWP Number: AL-90-360-001

Program Scope: Development and application of advanced solid-state nuclear magnetic resonance (NMR) methods to elucidate the nanometer-scale structure and dynamics of heterogeneous polymer-based materials under the following types of conditions: Ionomers as used, for instance, in all-solid H₂/O₂ fuel cells; Polymers intercalated in layered silicates; Biological and biomimetic apatite-polymer nanocomposites.

Major Program Achievements (over duration of support):

Improved Characterization of Heterogeneous Polymers: New ¹H spin diffusion NMR methods for characterizing heterogeneities in multicomponent polymer materials, on the 0.5 - 50 nm scale, have been introduced. They provide improved contrast through ¹³C evolution and detection, and improved accuracy by calibration of local spin diffusion coefficients. Sensitivity enhancement (4 - 10-fold) has been achieved in various NMR experiments by indirect ¹H detection, signal refocusing, or multiple alternating depolarization.

NMR of Fluoropolymers: NMR methods for characterizing fluorinated polymers, in particular the ionomer Nafion used in fuel-cell polymer-electrolyte membranes, have been advanced. High-resolution ¹³C NMR of Nafion and PTFE (Teflon) was achieved for the first time, by fast magic-angle spinning and pulsed ¹⁹F decoupling; it characterizes chain conformational order. We have detected uniaxial chain rotations in Nafion and Teflon, which enable our CODEX experiment with ¹⁹F spin diffusion to characterize chain-packing order. The experiments reveal that Nafion backbone chains form rotating, conformationally ordered helices that aggregate on the 1-nm length scale, but with limited orientational order. The branch points are relatively immobile, while the anionic sidegroups move significantly in the presence of water. On the basis of quantitative fits to the NMR and small-angle scattering data, we have introduced a new "alternating-curvature" model of Nafion, which will provide the basis for further studies of the origin of the selective cation permeability of Nafion membranes.

Heterogeneous para/ferromagnetic polymer materials. Many polymer-based materials contain para- or ferromagnetic particles. New insights into their effects on the NMR of the polymer matrix have been obtained.

Organic-Inorganic Nanocomposites: Heteronuclear NMR correlation methods have been used to analyze the chemical structure at and on both sides of the organic-inorganic interfaces in silicate- and apatite-polymer nanocomposites. Several new NMR approaches, including Heteronuclear Recoupling with Dephasing by Strong Homonuclear Interactions of Protons (HARDSHIP), have yielded the thickness of apatite nanocrystals in bone and the depth of carbonate and hydroxide ions from the organic-inorganic interface. The composition of the nanocrystal surface, in terms of protonated phosphates and bound water, has been studied in detail. Variations in apatite composition, such as OH⁻ concentrations, exceed variations in crystal thickness for different species.

Program Impact:

This work has provided insights into the microscopic origins of macroscopic properties of heterogeneous polymers; hopefully, this will eventually lead to improved materials. The NMR techniques developed by our group have been and will be used worldwide by other NMR groups.

Interactions (External):

University of Southern Mississippi, Hattiesburg.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

John H. Dillon Medal of the Polymer Division of the American Physical Society (KSR '01). Total of 9 invited talks and 12 refereed publications in this topic area since 2002.

Personnel Commitments for FY2005 (Actual Effort):

K. Schmidt-Rohr (50%); Q. Chen (50%); A. Rawal (45%); E. Levin (50%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$275,000

FY04 BA \$270,000

FY05 BA \$245,000

Laboratory Name: Ames Laboratory
B&R Code: KC0203

FWP and/or possible subtask under FWP:

Materials Chemistry and Biomolecular Materials: 8. Bioinspired Materials: Aptamer-Mediated Templates for Hybrid Elastic Nanostructures

FWP Number: AL-90-360-001

Program Scope: Creation of a new class of biomimetic hybrid materials involving magnetite nanocrystals embedded in hierarchically self-assembling polymers. Controlling nanoscale magnetite synthesis using bacterial mineralization proteins and using DNA/RNA aptamers for achieving specificity of non-covalent binding within the polymer. Investigation of these novel materials and processes using experimental characterization tools as well as theoretical approaches combining modern polymer theory and the theory of micro-magnetism.

Major Program Achievements (over duration of support): We have successfully cloned the sequence for the bacterial mineralization protein mms6 from *M. Magneticum* and expressed it in *E. Coli*. Since most of the recombinant mms6 protein was insoluble and found in inclusion particles, the protein was renatured and successfully separated by affinity chromatography. Both the native as well as refolded mms6 proteins were found to facilitate formation of uniform cubo-octahedral nanocrystals of magnetite in solution with sizes of about 50 nm, as seen by transmission electron microscopy. It is very difficult to synthesize nanocrystals with similar size and morphology by using other synthetic techniques. The magnetite nanocrystals obtained exhibited strong superparamagnetic behavior, which is typical for monodomain nanoparticles. The self-assembling polymer to be used for templating these nanocrystals was synthesized as described in subtask 6. In the presence of the polymer gel, the formation of these magnetite nanocrystals was found to be much more controlled than in free solution. X-ray photoelectron spectroscopy indicates that the protein is associated with the magnetite nanocrystals. The nanocrystals formed in the presence of ferritin, another iron-binding protein as control, did not exhibit the uniform sizes and shapes seen in the presence of mms6. DNA and RNA aptamers are being developed to bind to mms6 as well as the self-assembling polymers. Initial temperature-dependent magnetic measurements of these polymer-nanomagnet composites showed magnetic transitions corresponding to the temperature-induced self-assembly processes in the polymeric matrix.

Program Impact: The use of bacterial mineralization proteins to create uniform, monodisperse, monodomain nanocrystals of magnetite *in vitro* represents a new paradigm for nanocrystal synthesis and processing using bioinspired methods. The non-covalent linkages and the hierarchical self-assembly processes enable bottom-up approaches for materials design.

Interactions:

Argonne National Laboratory

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

NSF-CAREER award (SKM, '00); ISU Early Excellence in Research award (SKM, '01); MIT's Technology Review's "Top 100 Young Innovators" list (SKM, '02); ISU College of Liberal Arts and Sciences Award for Excellence in Research Creativity (GAK, '01); ISU University Professor (GAK, '04); ISU Regents Faculty Excellence Award (GAK, '04); Federated Laboratories Consortium Distinguished Service Award (GAK, '05); MIT's Technology Review "Top 100 Young Innovators" list -TR100 Award (BN, '03); ISU Early Excellence in Research Award (BN, '03); 3M Faculty Award (BN, '03); Fellow of the American Physical Society (PCC '02); Divisional Associate Editor for Phys. Rev. Lett. (PCC '02).

Personnel Commitments for FY2005 (Actual Effort):

S.K. Mallapragada (20%); M. Nilsen-Hamilton (20%); P. Palo (25%); J. Banerjee (15%); L. Wang (15%); G.A. Kraus (5%); T.-W. Guo (20%); B. Narasimhan (5%); T. Prozorov (25%); D. Bazylnski (5%); T. Williams (20%); P. Canfield (5%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$0

FY04 BA \$0

FY05 BA \$350,000

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-01

FWP and possible subtask under FWP: Solid State Physics, X-ray and Neutron Scattering

Neutron scattering from correlated electron materials

FWP Number: AL-90-540-001

Program Scope: A variety of neutron scattering techniques are used to study structure, dynamics, and magnetism in hard and soft matter. We explore structural phase transitions, lattice dynamics, magnetic structures, and magnetic excitations in exotic materials; such as superconductors, low dimensional magnetic systems, magnetostriptive and shape memory materials, ionic conductors, correlated electron systems and complex magnetic materials. We also apply reflectivity and inelastic scattering techniques to investigate thin organic films and magnetic molecules.

Major Program Achievements (over duration of support):

Inelastic neutron scattering under applied magnetic fields of cubane-type deuterated magnetic molecule $[\text{Cr}_8\text{O}_4(\text{C}_6\text{D}_5\text{COO})_{16}]\cdot 4\text{CD}_3\text{CN} = \{\text{Cr}_8\}$ revealed the low-lying magnetic excitation spectrum of this system. The molecule contains eight $s = 3/2$ Cr^{3+} centers that are isotropically coupled. The magnetic behavior (elastic and inelastic scattering) of Li-orthophosphates were determined. Lattice dynamical studies were completed on a series of giant magnetostriptive Fe-Ga solid solution alloys and on one in a series (Al) of shape memory/martensitic alloys (NiMnM, M=Al, In, Sn). Magnetic structures as a function of composition and phase were determined for several complex materials and intermetallics. A new program to study lattice and spin dynamics near metal-insulator transitions has revealed interesting magnetic and lattice excitations in the YBaFe_2O_5 and YBaCo_2O_5 systems. This work has been bolstered by new powder and single-crystal sample preparation capabilities within the group. A newly commissioned liquid surface diffractometer at the Advanced Photon Source synchrotron has been utilized to study biomimetic membranes. The recently reinstalled and upgraded HB1A Ames Laboratory triple-axis spectrometer at the HFIR has become part of the user program at that facility. We also continue our active participation in the IDT's for the HYSPEC, SEQUOIA, and ARCS spectrometers for the Spallation Neutron Source (SNS), as well as in the design of CG-1 cold-neutron triple-axis spectrometer at the HFIR. As part of the preparation for the SNS, we continue to develop parallel algorithms for analysis of neutron scattering using sophisticated and appropriate models for phonon and spin wave systems.

Program Impact:

Our neutron scattering findings in cuprates and related oxides help understand the complex interplay between magnetism, lattice dynamics and electronic behavior. Neutron spectroscopy of magnetic molecules is crucial for testing theoretical predictions; the spectrum of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ confirms theoretical predictions based on a 3-sublattice effective Hamiltonian developed in Ames. Neutron structural and magnetic studies of Li-phosphates ionic conductors help understand the effects of substitutions/vacancies on ionic conductivity, and elucidate the magneto-electric effect. X-ray and neutron scattering from bio-organic films are crucial for establishing bio-mimetic routes to novel materials. The Ames Laboratory liquid surfaces diffractometer at the Advanced Photon Source has been in demand by scientists with diverse interests, such as physicists, chemists, biophysicists, and chemical engineers. HB1A, even though a side port instrument, is the one of the most reliable instruments at the HFIR and has productivity rivaling major international triple axis instruments.

Interactions: Internal— Materials Preparation Center, numerous Ames Lab groups dealing with magnetic materials (Johnston, Canfield, Kögerler, Gschneidner, Goldman, Tsukruk, Lograsso, Schlagel, Pecharsky, Bud'ko,)

External— ORNL, BNL, LANL, NIST, Universities: California Irvine, Missouri, Johns Hopkins, Tennessee, CalTech, Oslo (Norway), Leipzig (Germany), Geneva (Switzerland), Bilbao (Spain), Campinas (Brazil), Paul Scherrer Institute (Switzerland).

Recognitions, Honors and Awards (at least in some part attributable to support under this program)

D. Vaknin – Executive Committee, SNS and HFIR users' group. Neutron Biology Task Force.

J. L. Zarestky- Executive Committee SNS/SEQUOIA IDT, HYSPEC IDT member.

R. J. McQueeney – Executive Committee SNS/ARCS and HYSPEC. SEQUOIA IDT member.

Personnel Commitments for FY2005 to Nearest +/- 10%:

D. Vaknin (100%), J. Zarestky (90%), R. McQueeney (20%), Postdocs: Chang(100%), Garlea(75%), Li(100%), Wei(50%), Yan (50%), and 1.5 students(100%).

Authorized Budget (BA) for FY03, FY04, FY2005:

FY03 BA \$840k

FY04 BA \$740k

FY05 BA \$1047k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-01

FWP and possible subtask under FWP: Solid State Physics, X-ray and Neutron Scattering, X-ray Physics

FWP Number: AL-90-540-001

Program Scope:

The structural characterization of materials and the investigation of structural changes associated with, or leading to, novel behavior of materials. The emphasis has been on the development of techniques, such as magnetic x-ray scattering and more recently, studies of liquid structure using a novel electrostatic levitation furnace in the MUCAT sector at the APS.

Major Program Achievements (over duration of support):

Most recently, the group has concentrated their efforts on the origin and physics of the x-ray resonant magnetic scattering amplitudes and has shown that consideration of spin-orbit coupling in the 5d band of rare earth compounds is critical to understanding the systematics of resonant scattering and dichroic intensities in rare earth compounds. They have recently shown that the structure of antiferromagnetic domains in rare-earth compounds may be studied by resonant magnetic scattering using linearly polarized x-rays. This will have a strong impact on: (1) Investigations of compounds with proposed multiple-q structures since the scattering at each wavevector for a single domain may be studied; and (2) Complex, multicomponent magnetic systems such as rare-earth/transition metal compounds where both species carry a moment. They have also succeeded in the first magnetic x-ray powder diffraction measurements of rare-earth compounds using polarization analysis to separate the weak magnetic signal from the stronger charge diffuse background. This is important for preliminary measurements of complex magnetic compounds with low magnetic symmetry, presenting magnetic peaks that are difficult to locate using single crystal samples.

Program Impact:

Graduate on average one student per year, trained in x-ray scattering techniques. The magnetic scattering program is arguably one of the most productive efforts in the world, particularly in the areas of new magnetic scattering techniques, the elucidation of the origin of the resonant magnetic scattering amplitudes, and the use of magnetic scattering for *ab-initio* magnetic structure determination. In addition, together with groups from Washington University, the University of Massachusetts (Amherst) and NASA's Marshall Space Flight Center, the x-ray scattering group has had a strong impact on investigations of liquid structures using an electrostatic levitation furnace to achieve deep undercooling of liquid metals, intermetallic compounds and semiconductors (Si).

Interactions:

Internal – Strong interactions with groups in Materials Chemistry and MEP, (e.g. the high temperature diffractometer was built with M. Kramer and R.W. McCallum (MEP)), on magnetic scattering there is strong interactions with the theory group of B. Harmon.

External – XOR (Argonne), Washington University, NASA MSFC, University of Massachusetts.

Recognitions, Honors and Awards (in some part attributable to support under this program):

Goldman is a Fellow of the American Physical Society and Director of the MUCAT (Midwest Universities Collaborative Access Team) sector at the Advance Photon Source.

Personnel Commitments for FY2005 to Nearest +/- 10%:

A. I. Goldman (PI-25%), Andreas Kreyssig (PD-50%), Students: Jong-Woo Kim (100%), Lizhi Tan (50%), technician: Marc McGinn (25%).

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$250k

FY04 BA \$308k

FY05 BA \$268k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-01

FWP and possible subtask under FWP: Solid State Physics, X-ray and Neutron Scattering
MUCAT –Midwest Universities Collaborative Access Team

FWP Number: AL-90-540-001

Program Scope: The Midwest Universities Collaborative Access Team (MUCAT) was organized for the purpose of developing and operating a sector (insertion device and bending magnet lines) at the Advanced Photon Source. MUCAT saw light in the First Optics Enclosure in February 1998. Experiments on the main undulator line began late in FY99. The undulator line presently consists of two experimental stations in tandem for x-ray studies in the 3-40 keV energy range. A high-energy side station (30-130keV), funded by FZ Juelich, allows simultaneous operations of the main line and side station. The construction of a bending magnet beam line is in progress.

This consortium brings together scientists from several universities, national and international laboratories with common interests in the use of synchrotron radiation for materials science research. The magnetic scattering and spectroscopy portion of the scientific program concentrates on resonant and nonresonant scattering studies of magnetic materials. Resonant and nonresonant magnetic x-ray scattering measurements offer important and complementary means of determining magnetic structures in materials which are ill-suited, by reasons of size or chemical composition, to traditional neutron measurements. Research efforts in the surface scattering program are centered on the study of the kinetics and growth of 2-dimensional systems, the role of defects in epitaxy, ordered non-epitaxial overlayers, phase transitions and investigations of liquid surfaces. A liquid surface diffractometer is used to probe the chemistry and physics of monolayer films at liquid surfaces. It can test and validate realistic models of biological membranes and their reaction to various stimuli and environments. High energy x-rays are used for in-situ studies of materials processing using a custom designed high temperature furnace constructed at the Ames Laboratory and for studies of pair distribution functions of poorly or partially ordered structures.

Current Capabilities

The four-circle diffractometer and liquid surface diffractometer in 6-ID-B have been declared operational (November 2000 and November 2001 respectively), and are already well subscribed by general users. The commissioning of the high-energy side station (6-ID-D) and surface science station (6-ID-C) were completed in FY03. At the same time, we are developing the bending magnet beam line (6-BM-A,B).

Program Impact: Publications and invited talks about MUCAT research have been growing rapidly (85 publications since 2001 including 6 Physical Review Letters and hundreds of talks). The Sector serves a wide range of investigators both within and external to the MUCAT collaboration working in the general area of materials science. Highlights over the past year include: (1) A new investigation of the structure of undercooled liquid Si providing new evidence that there is no liquid-liquid phase transition in this system; (2) The first demonstration of resonant magnetic scattering using linearly polarized x-rays to image antiferromagnetic domains and; (3) The first magnetic x-ray powder diffraction measurements on rare-earth compounds.

Interactions:

Internal—Solid State Division, Alloy Behavior and Design Group, X-ray Research and Applications Group, Structural Ceramics Group.

External— Member institutions: Ames Laboratory/Iowa State, U. of Missouri, Georgia Tech, Washington U., U. of Wisconsin, Kent State, SUNY Stony Brook, Michigan State, and FZ Juelich in Germany.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):

Review by APS Scientific Advisory Committee last year rated the science as “Outstanding”.

Personnel Commitments for FY2005 to Nearest +/- 10%:

Douglas Robinson (100%), Didier Wermeille (100%), Eric Zoellner (100%), Philip Ryan (100%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$482k

FY04 BA \$460k

FY05 BA \$567k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics, Experiment.
Optical Properties and Photoemission Spectroscopy of Solids and Surfaces

FWP Number: AL-90-540-002

Program Scope:

Angle-resolved photoelectron spectroscopy is used to elucidate the electronic structure and interactions in solids. Materials studied are generally metallic, and very often are systems in which electron correlations are very important. The program is developed on two parallel, but not disconnected tracks: high temperature superconductivity and heavy Fermion systems. The most pressing issues in high temperature superconductivity include investigation of the role of collective excitations, inhomogeneities, and relation between results from various experimental techniques. The study of heavy Fermion compounds concentrates on Ce- and U-based intermetallic compounds. The new approach in this effort is to systematically study the electronic structure of families of compounds that display heavy fermion behavior. Current samples include Ce₂Sb, CeSb₂, USb₂, RNi₂Ge₂ (R=Eu, Gd), RAgSb₂ (R=Y, La-Nd, Sm). Instrumental work includes developing a laboratory based ARPES microscope that allows studies of inhomogeneities and obtain momentum resolved spectra from polycrystalline samples of novel strongly correlated materials.

Major Program Achievements (over duration of support):

The major achievements include both advances in methodology of the technique and understanding of electronic properties of specific systems. First observation (Olson, Lynch) of the superconducting gap in any cuprate by photoelectron spectroscopy (or any technique). Early band mapping of two cuprates. Establishment of a Fermi Surface in the cuprates. First demonstration of dispersion, hence band-like states, in a quasicrystal. Showed value of using changes in energy dependent matrix elements and the cross sections to isolate details of the electronic structure. First recognition (simultaneously with IBM group) that both peaks in Ce and Ce compounds arise from the 4f electron. Demonstration of weak dispersion in 4f bands CeSb, LaSb, Ce₂Sb (via hybridization). The dispersion on one of the two Ce sites in Ce₂Sb is very clear. The second site is much more localized (on one site the Ce-Ce distance is much less than in the metal, and on the other site it is greater). The situation for LaSb is a little softer. There is no inherent f character in La. At resonance, we see what appears to be f character, which can only come from decomposition of a heavily hybridized valence band state. Development of new technique – AutoCorrelated (AC) ARPES that allows direct identification of elastic scattering processes. We are currently working on expanding this to the inelastic channel.

Program impact:

Characterization of electronic states, often including band mapping, led to better understanding of correlation in Ce-based systems. Convinced others of importance of dipole matrix elements. Early band mapping of cuprates and observation of superconducting gap attracted wide interest. Contribution to methodology of ARPES data interpretation.

Interactions:

Internal: P. C. Canfield, T. Lograsso, V. Antropov, B. N. Harmon

External: J. J. Joyce (LANL), J.-S. Kang (Catholic University of Korea), Juan Carlos Campuzano (University of Illinois at Chicago), Mike Norman (Argonne National Laboratory) and Mohit Randeria (Ohio State University)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

82 invited talks since the inception of the photoelectron spectroscopy program. Olson and Lynch are both Fellows of the American Physical Society. Kaminski was co-organizer of workshop “Frontiers in Soft X-ray, VUV and Infrared Research” and a chairman of 38th SRC Users Meeting. Kaminski has given 7 invited talks in 2005.

Personnel Commitments for FY2005 to Nearest +/- 10%:

D. W. Lynch (Now 0%), C. G. Olson (100%), Adam Kaminski (17%), Joong-Mok Park, Post Doc (100%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$230k

FY04 BA \$300k

FY05 BA \$350k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experiment
Control of Atomic Scale Growth on Surfaces

Program scope:

Characterization and control of atomic scale structures grown on clean surfaces. Two complementary techniques, Scanning Tunneling Microscopy (STM) and High Resolution LEED are used. Since the growth of self organized low dimensional nanoscale structures holds the promise for revolutionary technological applications, the scope of our program is to discover novel routes to the self organization. In collaboration with theoretical groups worldwide we aim in attaining understanding of the factors controlling the energetic stability and in modeling the kinetics of the grown structures. The ultimate goal is to use this information to grow in a predictable custom-made nano materials of uniform dimensions.

Major Program Achievements (over duration of support):

In the past year we have worked on several problems. (i) Uniform Pb nanowires grown on Si(111)-In(4x1) with both height and width controlled. The height is controlled by Quantum Size Effects (QSE) (as shown by our pioneering discovery of uniform height Pb islands 4 years ago) and by the anisotropic surface strain on the reconstructed surface. (ii) In collaboration with Miceli (Missouri) and Conrad (Georgia Tech) we have discovered non-classical coarsening kinetics of the Pb/Si(111)-7x7 uniform height islands. The time evolution is extraordinarily fast and can account for the self organization at low temperatures. (iii) In collaboration with the local theorists (Ho and Wang) we have shown that the diffusion barrier on top of the uniform height islands oscillates with height due to QSE. (iv) In collaboration with Chvoj (Czech Academy of Sciences) we have developed a sophisticated Monte Carlo program to deduce the potential energy surface controlling the Pb island formation. (iv) In collaboration with Zaluska Kotur (Polish Academy of Sciences) and Gortel (Alberta) we explained the very rapid formation of the numerous "Devil's Staircase" (DS) phases we discovered in Pb/Si(111) by calculating the diffusion coefficient in a system with long range interactions. (v) In collaboration with Chvoj we are organizing the International Workshop on Physics and Technology of Thin Films, Prague 2006 (IWTF2) to be held in Prague June 2006.

Program Impact: Our work on surface diffusion has been recognized internationally by two major international conferences (Rhodes, Greece in 1996, and Prague in 2000). An invited chapter on surface diffusion is included in the second edition of the book, "*Diffusion in Condensed Matter*" editors: J. Karger, P. Heitjans, R. Haberlandt. We have given, by invitation, four lectures in the 41st Karpacz Winter School of Theoretical Physics *Diffusion and Soft Condensed Matter Physics* February 2005. Our discovery of the uniform height island growth on Pb/Si(111) has generated interest with six other groups worldwide currently working on this system in Taiwan, Illinois Oak Ridge, Chou, Georgia Tech, Poland, Berlin.

Interactions: Local: C. Z. Wang, K.-M. Ho, J. Schmalian, C. Olson, D. W. Lynch, A. Kaminski;

Outside within last year with submitted papers: Ed Conrad (Georgia Tech), P. Micelli (Missouri), Z. Chvoj (Academy of Sciences, Czech Republic), Zaluska Kotur (Polish Academy of Science) Gortel (Alberta), Argyrakis (Thessaloniki); Outside collaborators over the last three years: T. Rahman (Kansas State) Z. Zhang (Oak Ridge), J. Wendelken (Oak Ridge) M. Henzler (Hannover, Germany), M. Hon-von-Hogen (Essen Germany), M. Jalochowski (Lublin, Poland), K. Roos (Bradley).

Recognition:

1 *Physical Review Letter* and 2 *Rapid Communications* in the last 3 years; 11 papers published and 5 submitted last year; 14 invited talks at international meetings and institutions within last year; co-edited two conference books; Tringides became an APS Fellow in 2003.

Personnel Commitments for FY2005 to Nearest +/-10%:

M. C. Tringides(25%), M. Hupalo(100%), Students: M. Yakes (50%), J. Chen (25%).

Authorized Budget (BA):

FY03 BA \$244k FY04 BA \$239 FY05 BA \$250k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics – Experiment
New materials; NMR and NQR investigations of new materials and phases

FWP Number: AL-90-540-002

Program Scope: Synthesis and study of new and improved oxide and other materials with potentially novel electronic and/or magnetic properties. Characterization of the materials using x-ray diffraction, magnetization, magnetic susceptibility, specific heat, electronic transport, thermal analysis, and NMR and NQR measurements, to understand, e.g., the electronic structure and magnetic properties of new superconductors and strongly correlated metals and alloys, the hopping dynamics of light ions in fast ionic conductors, and the classical and quantum spin dynamics in single molecule nanomagnets. Theoretical modeling of the properties. Provision of high-quality single crystal and polycrystalline samples to other groups for measurements of additional properties.

Major Program Achievements (over duration of support): 1) Extended our ^7Li NMR measurements of our novel *d*-electron heavy fermion spinel-structure compound LiV_2O_4 down to 0.5 K, which further confirmed the heavy fermion nature of this material. 2) Discovered novel properties of magnetic defects in LiV_2O_4 and developed a model to understand the data. 3) Discovered how to grow single crystals of LiV_2O_4 using flux growth techniques and how to vary the magnetic defect concentration in the crystals by annealing them. 4) Searched for other new superconducting and/or metallic oxides. 5) Developed a new model for the hopping dynamics in glassy fast ion conductors. 6) Identified the nuclear-spin lattice relaxation mechanism at low temperatures in magnetic nanomagnets as due to a strong collision mechanism induced by incoherent quantum tunneling of the magnetization, which is a new tool to directly measure the tunneling rate. 7) Explained the NMR signal loss in molecular magnets such as Mn_{12} and Fe_8 in terms of fluctuations of the magnetization due to spin-phonon interactions.

Program impact: Much of the progress in condensed matter physics is driven by the discovery of new or better materials. Our discovery of *d*-electron heavy fermion behavior in LiV_2O_4 continues to attract widespread experimental and theoretical attention. Our recent discovery of novel properties of magnetic defects in this compound helped us maintain our world leadership in the area of *d*-electron heavy fermion physics. Our model for the ^7Li NMR relaxation when magnetic defects are present in the structure has wide implications for understanding the dynamics of a wide range of glassy materials. We established parameters over a wide range of temperatures describing the ion dynamics in fast ion conductors. Our group has continued to be international leaders in the application of NMR methods to the study of magnetic molecules. Our methods and interpretation paradigms developed in the study of magnetic molecules have been adopted by other research laboratories worldwide.

Interactions: Internal - Ames Lab (Schmalian, Kaminski, Lake, Luban, Canfield)-CMP, (Cook, Russell, Martin)-MEP; External – Brookhaven National Lab, U. Hamburg, U. Tokyo, Kyoto U., ETH Zürich, U. Pavia, U. Hokkaido, ILL Grenoble, U. Florence, U. Modena, Catholic U. Seoul, Boston College

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Distinguished Professor of Liberal Arts and Sciences, Iowa State U. (Johnston); Fellow of the American Physical Society (Johnston, Borsa); Named a "Highly Cited Researcher" by the Institute for Scientific Information, 2004 (Johnston); Borsa: Fellowship, Japan Society for the Promotion of Science (1998), Member, Program Committee, Internat. Conf. on Magnetism, Rome, 2003; invited talk at international conference, Spring 2005.

Personnel Commitments for FY2005 to Nearest +/- 10%:

D. C. Johnston (group leader) 17%; F. Borsa (group leader) 17%; A. Niazi (100%), Y. Singh (100%), and M. Belesi (8%) (postdocs); Z. H. Jang (17%), R. Vincent (10%), and B. J. Suh (17%) (visiting scientists); S. Das (12%), X. Zong (50%), and S.-H. Baek (17%) (graduate students). Note: Borsa retired during 20

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$195k

FY04 BA \$181k

FY05 BA \$252k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experimental
Photophysics of luminescent organic semiconductors and organic light-emitting diodes (OLEDs)

FWP Number: AL-90-540-002

Program Scope:

Fabrication & studies of π -conjugated thin films and OLEDs. The films are studied by photoluminescence (PL)- and PL- and photoinduced absorption (PA)-detected magnetic resonance (PLDMR and PADMR, respectively). The OLEDs are studied by current- and electroluminescence (EL)-voltage measurements, and by EL- and electrical current-detected magnetic resonance (ELDMR and EDMR, respectively).

Major Program Achievements (over duration of support):

Completion and publication in PRL of our novel double-modulation PLDMR (DM-PLDMR) study of an archetypal luminescent polymer. That study, and the joint PLDMR and thermally stimulated luminescence measurements, directly contradict the “delayed PL” mechanism previously proposed to explain the PLDMR and PADMR, and its underlying assumption that the yield of singlet excitons (SE) in polymer OLEDs is >25% and may be as high as 60%. The DM-PLDMR also supports the scenario that the central spin-dependent interaction in luminescent π -conjugated materials is the annihilation of triplet excitons (TE) by polarons. This interaction is very significant since under normal operating conditions the steady-state population of polarons and TEs is much higher than that of SEs.

We have discovered conditions under which the EL spectrum of certain OLEDs is spectrally narrowed, to as little as 7 nm. We are currently investigating this phenomenon extensively to elucidate its nature.

We are rapidly developing the new platform we invented for luminescent chemical and biological sensors and sensor arrays, in which the OLED light source is structurally integrated with the sensor film with an OLED light-source. We have obtained considerable funding from NASA, NSF, and NIH for practical development of this new platform.

Program impact:

Our ODMR studies support the conclusion that the maximal internal quantum efficiency of all fluorescent small molecular and polymer OLEDs is ~25%. They also identified two PL and EL quenching mechanisms which strongly impact the PL of films and EL of OLEDs at high excitation densities. Our other studies on OLEDs underpin the science for the development of OLEDs for solid-state lighting, low-cost ultrafast pulsed light-sources, spectrally narrowed emission, and a new platform for chemical and biological sensors and microsensor arrays.

Interactions:

External - Department of Electrical Engineering, MIT; Chemistry Dept, Princeton Univ; Chemistry Dept, Bowling Green State Univ; Chemistry Dept, UCLA; Appl Phys & Mat Sci Dept, City Univ, Hong Kong.

Local – R. Shinar & V. Dalal, Microelectr. Res. Cntr; L. Tabatabai, Biochem., Biophys., & Molec. Bio.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

23 invited talks from Oct 1, 2002 till Sept 30, 2005; 11 papers published, 1 accepted, 3 submitted in FY 05.

2004 Iowa State University Foundation Outstanding Achievement in Research Award, 2004 APS Fellow.

Personnel Commitments for FY2003 to Nearest +/- 10%:

J. Shinar, PI, 25%; Postdoctoral Fellows, 1.0 FTE; Graduate students, 4.0 FTE

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$220k

FY04 BA \$220k

FY05 BA \$305k

Laboratory Name: Ames Laboratory

B&R Code: KC020202

FWP and possible subtask under FWP: Solid State Physics, Experimental
Correlated states in magnetic materials

FWP Number: AL-90-540-002

Program Scope:

Design, discover, grow and characterize novel materials with exotic / interesting physical properties (generally electronic / magnetic).

Major Program Achievements (over duration of support):

Over the past three fiscal years this program has been studying a wide range of intermetallic systems that manifest magnetic and / or superconducting ground states. Since January 2001 this program has been a world leader in the synthesis and characterization of MgB₂, the binary intermetallic superconductor with T_c~40 K. We have delineated the mechanism of the superconductivity, range of the superconducting state and salient physical length scales, and demonstrated a simple synthetic route to making powders, wires and films. More recently (PRL 2004) carbon has been identified as a key dopant for doubling the upper critical magnetic field (from 16 T to 32 T). We also systematically studied the effects of neutron damage (PRB submitted). In addition, this program continues to be a world leader in the study of the RNi₂B₂C family of magnetic superconductors, the growth and properties of single grain quasicrystals (including the magnetic RMgZn family), and metamagnetic transitions and spin-glass properties in anisotropic local moment systems. During FY04 we identified YbAgGe (a member of the RAgGe family that we have been studying) as the second known, Yb-based, field induced quantum critical point compound. This discovery has generated great excitement and spawned new collaborations throughout the world (France, England, Canada, Germany, Japan).

Program impact:

120 publications between Jan. 2003 and Nov. 2005 (as well as several patents filed on the processing of MgB₂) 33 Physical Review B, 9 Physical Review Letters, as well as smaller numbers of papers in journals such as Physica C, Physica B, J. Alloys and Comp., Physics Today, Physics World, and Scientific American (translated into a variety of languages including German and Chinese). This program's work is very highly cited. For example the work on MgB₂ (less than 5 years old) has been cited over 1400 times. Given the recent nature of the research, this is a phenomenal citation rate, indicating a high impact on the field.

Interactions: (internal) A. Kaminski, R. Prozorov, V. Antropov, F. Borsa, D. Finnemore, A. Goldman, B. Harmon, V. Kogan, R. McQueeney, J. Schmalian, T. Lograsso, J. Zarestky, J. Corbett, C. Jenks, P. Thiel, M. Kramer, K. Dennis, R. McCallum, G. Miller, S. Malapragada (external) Riso, Stanford, National High Magnetic Field Lab (LANL and Florida), ESRF (Grenoble), ILL (Grenoble), CEA (Grenoble), CNRS (Grenoble), Brookhaven National Laboratory, ISIS (England), ETH (Zurich), MPI (Dresden), as well as dozens of other labs and universities throughout the world.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Fellow of the American Physical Society (PCC); Divisional Associate Editor for Phys. Rev. Lett. (PCC).
Over 30 invited talks / colloquia, including invitations to write articles for Physics World, Physics Today, Scientific American and Encyclopedia entries on MgB₂

Personnel Commitments for FY2005 to Nearest +/- 10%:

P. Canfield (15%), S. L. Bud'ko (95%), visiting scientists: Y. Jennsen (100%), M. Angst (100%), G. Lapertot (50%), graduate students: Emilia Morosan (100%), Derek Wilke (100%), S. Jia (100%), M. Tillman (50%), E.D. Mun (50%), N. Ni (50%), undergraduate students: Stephanie Law, Josh Friedrich

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$588k

FY04 BA \$621k

FY05 BA \$751k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics - Experiment

Correlated states in magnetic materials – magneto-optics

FWP Number: AL-90-540-002

Program Scope:

This project was initially motivated by new capabilities for studying the optical properties of magnetic materials. With David Lynch retiring, experiments covering the low energy range of the optical spectra are made by external collaborators. This project also began with a strong experimental component for the synthesis of new materials. Paul Canfield was hired and his very successful efforts are now funded in a separate group. More recently, magnetic x-ray scattering experiments become a valuable new tool, and there are a number of collaborative projects involving the x-ray group of Alan Goldman. Materials studied are obviously magnetic. Most contain a rare earth, or a transition metal, or both. First principles electronic structure calculations are performed to understand the often subtle MO spectra and to assess the degree and importance of correlated d- and f-electron states.

Major Program Achievements (over duration of support):

Measurement of Kerr spectra for over a dozen intermetallic compounds and successful calculation of such spectra. Observation of a metamagnetic (ferro- to antiferromagnetic) transition in $\text{Ce}(\text{Fe}_{0.9}\text{Co}_{0.1})_2$ by magneto-optic spectroscopy and MOKE spectrum in AF phase. We made the first calculations of MO spectra employing the LDA+U technique for treatment of correlated electron states. The calculations were very successful for magnetite (Fe_3O_4), and for a series of mixed-valent materials (Tm monochalcogenides, SmS, ThB6, etc.). Spectra were also calculated for planned x-ray magnetic circular dichroism (XMCD) experiments for $\text{Gd}_5\text{Si}_2\text{Ge}_2$, the complex magnetic refrigeration material being investigated in Ames. MO spectra for the shape-memory compound Ni_2MnGa were obtained for both cubic and tetragonal phases. We wrote a 500 page book (published in 2004 by Kluwer), presenting the techniques and results of over 20 publications in the last few years on MO and XMCD calculations. In last few months we showed the simple atomic models for the L_3/L_2 intensities for rare earths (in XMCD spectra) were not correct, but full relativistic band structure calculations agreed with experiment and suggested new insights.

Program impact:

Systematic study of several series of compounds shows rare-earth 4f-states rarely participate directly in MOKE spectra, but their moments polarize other electrons. The off-diagonal component of the dielectric function, proportional to the magnetization, can be calculated rather accurately as long as 4f states do not lie within a few eV of the Fermi level, or if the LDA+U technique is used to account for the strong correlations of the 4f electrons. The agreement with experiment is impressive and lends strong support for the LDA+U approach for optical spectral analysis. The success of theory in experiment in this area is excellent and we have written and published a book gathering together a large number of results. The XMCD work on rare earths is widely recognized and highly cited.

Interactions:

Internal: T. Lograsso, P. C. Canfield, A. Goldman; External: J.-Y Rhee (S. Korea), V. Antonov (Kiev)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP):

Lynch and Harmon are Fellows of the APS. 15 invited talks in last three years.

Book: "Electronic Structure and Magneto-Optical Properties of Solids", V. Antonov, B. Harmon and A. Yaresko, (Kluwer, Netherlands, 2004).

Personnel Commitments for FY2005 to Nearest +/- 10%:

D. W. Lynch (0%), B. Harmon (5%), V. Antropov (30%), V. Antonov (visiting scientist, Kiev, 30%), J.Y. Rhee (visiting professor, 10%), JoonMok Park (student, 50%).

Authorized Budget (BA) for FY03, FY04, FY05

FY03 BA \$109k

FY04 BA \$80k

FY05 BA \$100k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experiment
Low Temperature Phenomena

FWP Number: AL-90-540-002

Program Scope:

Advanced electromagnetic measurements of novel superconducting and magnetic materials. Design and use of unconventional highly precise experimental methods in magnetism and superconductivity, including work at temperatures below 10 mK.

Major Program Achievements (over duration of support):

This new program started in July 2005. In three months, "The Superconductivity and Magnetism Low-Temperature Laboratory" has become operational with three experimental setups already taking data. More experiments are under development. In particular, a unique tunnel-diode resonator technique is currently used on a ³He refrigerator and first data are being collected. This technique measures dynamic magnetic susceptibility with unprecedented sensitivity of few pico-emu (at least four orders of magnitude better than SQUID magnetometers). It is based on a self-resonating LC circuit where the measured quantity is the shift of the resonant frequency. Another unique technique already established in the lab is magneto-optical visualization of magnetic fields at surfaces. The microscope utilizes Faraday rotation in a special transparent ferrimagnetic Bi-doped iron garnet which is placed in contact with the sample. In addition, the lab has extensive conventional experimental capabilities, including Quantum Design MPMS and PPMS systems. The MPMS has two SQUID circuits, hence capable of measuring vector magnetization, which enables direct study the effects of anisotropy.

In addition to continuing our previously established research programs (superconducting and magnetic nanocomposites, pattern formation and topological hysteresis in type-I superconductors, mechanisms of superconductivity in unconventional superconductors, coexistence of superconductivity and magnetism) we are actively exploring internal collaborations. We already initiated joint projects with P. Canfield's group (novel magnetic and superconducting materials), D. Johnston group (magnetic defects) and M. Luban and P. Kogerler (magnetic molecules). In addition, we collaborate with Materials Chemistry and Biomolecular Materials research programs.

Program impact:

We are currently focusing on building and development of the experimental infrastructure. A large dilution refrigerator (with cooling power of 400 uW at 100 mK) is being acquired and this system will be used to study fundamental properties of magnetic and superconducting materials by various experimental techniques in the millikelvin region. This will significantly expand the experimental capabilities of the entire condensed matter program at Ames Lab.

Interactions: (internal) V. Antropov, S. Bud'ko, P. Canfield, J. Clem, D. Finnemore, A. Goldman, D. Johnston, V. Kogan, P. Kogerler, M. Luban, J. Schmalian, (external) U of Illinois, U of Maryland, U of Wisconsin, Louisiana State U, U of Sherbrook (Canada), U of Tokyo (Japan), U of Bristol.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

This is a new program, just starting in July 2005.

Personnel Commitments for FY2005 to Nearest +/- 10%:

Ruslan Prozorov (PI-17%); A postdoc and several students will be added in FY06.

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA

FY04 BA

FY05 BA \$100k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Condensed Matter Physics - Experiment
Magnetic Molecules

FWP Number: AL-90-540-002

Program Scope: Broad-based experimental and theoretical research program focused on magnetism at the nano-scale level as manifested in crystalline samples of magnetic molecules. The program is a closely coordinated interdisciplinary effort coupling skills in synthesis chemistry and condensed matter physics so as to achieve a comprehensive understanding of the major static and dynamic properties of molecules incorporating a finite number of exchange-coupled spin centers such as transition metal cations. The synthesis effort focuses on achieving both uncoupled and networked inorganic magnetic molecules of high symmetry. It also targets the controlled modification of a wide range of parameters (symmetries, spin quantum numbers, and exchange and anisotropy parameters) to allow systematic studies of various magnetic phenomena. Experimental studies utilize thermodynamic (especially magnetization at low temperatures and high magnetic fields), magnetic resonance (NMR, EPR), optical, and neutron scattering methods. Theoretical studies utilize analytical and computational methods applied to a wide variety of classical and quantum models of magnetic molecules.

Major Program Achievements (over duration of support):

Synthesis and full chemical and physical characterization of over 50 compounds of targeted magnetic molecules comprising 2 to 30 spin centers each, and additional specialized preparation of compounds for experiments. Quantum model giving the low-lying excitations of the giant Keplerate magnetic molecule $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and the theoretical intensity of inelastic neutron scattering in good agreement with experimental studies. Synthesis of $\{\text{Mo}_{72}\text{V}_{30}\}$, a spin _ version of $\{\text{Mo}_{72}\text{Fe}_{30}\}$. Scaling law for the magnetic field and temperature dependence of the proton spin-lattice relaxation rate in magnetic molecules with antiferromagnetic exchange. Comprehensive theoretical explanation of quantum decoherence and tunneling phenomena in the $\{\text{V}_{15}\}$ system. First-principles calculation of exchange constants in polyoxovanadate systems using electronic structure methods. Development of a quantitative theory of spin frustration, competing spin phases, and metamagnetic transitions in highly symmetric magnetic molecules, in some cases supporting long-lived metastable spin phases. Successful application of quantum Monte Carlo methods to non-frustrated magnetic molecules.

Program Impact:

Results of the Ames group have been published in more than 140 scientific articles on magnetic molecules between 1998-2005 and this has inspired scientific competition from other groups that pursue ramifications of our work. The growing numbers of collaborators in the U.S., Europe, India, and Japan reflects the fact that Ames has become a recognized focal point in this research area.

Interactions:

Internal – Other CMP groups within Ames Laboratory: D. Vaknin, R. Prozorov, and D.C. Johnston.

External - *Chemical synthesis*: University of Bielefeld (Germany), University of Manchester and University of Glasgow (UK); *ESR and high magnetic field methods*: Tohoku University (Japan); *Optical methods*: University of Tennessee; *NMR methods*: University of Pavia (Italy), Hokkaido University (Japan), Catholic University of Korea; *Neutron facilities*: Oak Ridge National Laboratory, ISIS (UK), Hahn-Meitner Institute (Germany); *Computational and Theoretical methods*: Oak Ridge National Laboratory, University of Applied Sciences-Bielefeld and University of Osnabrück (Germany), Catholic University of Nijmegen and University of Gronigen (Netherlands).

Recognitions, Honors and Awards (at least partially attributable to support under this FWP):

10-15 invited talks each year since 2001. Three articles published in *Physical Review Letters* in 2005.

Personnel Commitments for FY2005 to Nearest +/- 10%

V. Dobrovistki (20%), B. Harmon (PI-5%), P. Kögerler (PI-100%), M. Luban (PI-25%); Post-docs: M. Belesi(50%), J. Fielden(75%), and V. Garlea (25%); Visiting Scientists: F. Borsa, L. Cronin, Z. Jang, H-J. Schmidt, J. Schnack, C. Schröder, R. Vincent and R. Winpenny; Students: L. Engelhardt, and I. Rousochatzakis.

Authorized Budget (BA) for FY03, FY04, FY05 (project started in FY02):

FY03 BA \$550k FY04 BA \$550k FY05 BA \$550k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-02

FWP and possible subtask under FWP: Solid State Physics, Experiment
Photonic Band Gap (PBG) Materials

FWP Number: AL-90-540-002

Program Scope:

To design, model, and fabricate novel periodic structures resulting in photonic band gap crystals.

Major Program Achievements (over duration of support):

Design and development of directional antennas fabricated from cavities in PBG crystals operating at microwave frequencies in collaboration with Ekmel Ozbay's group at Bilkent University. Collaboration with Shawn Lin at Rensselaer Polytechnic Institute and Jim Fleming at Sandia National Laboratory on 3D waveguide networks in layer-by-layer silicon PBG crystals yielding high-performance crystals with large bandgaps. Theory of 3D metallic PBG crystals operating as filaments and fabricated by the group of Shawn Lin. Development of economical microtransfer molding method for fabrication of 3D layer-by-layer PBG crystals. Measurement of propagation loss in straight 3D PBG waveguide and perpendicular waveguide bends at microwave X-band frequencies. Development of tunable infrared emitter for efficient gas sensor devices in collaboration with scientists at Ion Optics. Design of 2D PBGs for waveguides and resonant cavities. Fabrication and detailed characterization of high-quality large-scale face-centered cubic layer-by-layer structures with fundamental stop bands ranging from 1.3 to 1.7 mm using direct laser writing (*Nature Materials*). Directional emission out of a subwavelength aperture in periodically corrugated metallic thin films and PBG waveguides (*PRL*). Spontaneous emission rates of dipoles in photonic crystal slabs evaluated.

Program impact:

Our group is one of the pioneers in the field of photonic crystals and continues to play a major international role in leading the development in this field. The work on metallic PBGs with exceedingly high thermal radiation may lead to very energy efficient lighting systems. Our results for emission out of subwavelength apertures hold promise for the integration of PBG waveguides with conventional optical systems.

Interactions:

Hong Kong University of Science and Technology, Sandia National Laboratory, Agilent Laboratory (Palo Alto), Bilkent University, Turkey, Ion Optics, Research Center of Crete, University of Twente, Netherlands, ETH, Zurich and University Karlsruhe, Germany.

Recognitions, Honors and Awards (attributable to support under this FWP or subtask):

DOE Energy 100 Award and DOE Science 100 Award, U. S. Dept. of Energy, organized three international conferences, 2 U.S. Patents issued, one in process. Soukoulis and Ho are Distinguished Professors, Iowa State Univ. and Fellows of the APS. Soukoulis is also a Fellow of AAAS and OSA, has a Senior Alexander von Humboldt Award, and is editor of the new journal *Photonics and Nanostructures: Fundamentals and Applications* since 2002.

Personnel Commitments for FY2004 to nearest +/- 10%:

Theory: K. M. Ho (15%), C. M. Soukoulis (8%), R. Biswas (50%), Postdocs: Z. Y. Li (10%), T. Koschny (20%), R. Moussa (10%); Students: Anan Fang (20%), Weitao Dai (20%), Lili Peng (20%), M. Kafesaki (unpaid), M. Li (25%).

Experiment: G. Tuttle (15%), K. Constant (9%), W. Leung (60%); postdocs: C. H. Kim (50%); students: Y-S. Kim (50%), J.-H. Lee (50%), J. Muehlmeier (50%), Lei Zhang (25%), Jiangfeng Zhou (25%), Bingnan Wang (25%), H. Kang (50%),

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$492k FY04 BA \$591k FY05 BA \$644k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Solid State Physics, Theory
Optical and Surface Physics

FWP Number: AL-90-540-003

Program Scope: To study the structure, dynamics, and electronic properties of solid surfaces using a combination of first-principles density functional calculations and tight-binding molecular dynamics simulations. Accurate and transferable environment-dependent tight-binding (TB) potentials are developed for accurate description of surface properties as well as genetic-algorithm schemes for efficient atomistic structure optimization on surfaces.

Major Program Achievements (over duration of support):

We performed first-principles calculations to study the diffusion barrier for a Pb adatom on Pb films of varying thickness. Our results show that the diffusion barriers are very low and show significant variation as a function of film thickness due to the quantum size effect. The calculated bi-layer oscillation of total energy provided an explanation of the dramatic difference in the growth morphology between islands with stable and unstable heights observed in STM experiments. (see Tringides section)

We have developed a Ag-Si TB potential that give an accurate description of the energetics of the $\sqrt{3} \times \sqrt{3}$ Ag/Si(111) surface structures. We are using this potential and our recently developed surface genetic algorithm approach to examine the structure of the Ag/Si(111) surface as a function of varying Ag coverage.

Program Impact:

Our theoretical studies interact closely with experimental studies both at Ames Lab and other institutions. The interplay between the theoretical and experimental studies provides a comprehensive picture of the structures and properties of surfaces. Understanding the structures, electronic properties and dynamical behavior of surfaces and interfaces has an important impact on our ability to grow and stabilize various surface-based nanostructures such as quantum dots and quantum wires.

Interactions:

Internal- M. Tringides, M. Hupalo (Ames Lab-CMP), External: C. Ciobanu (Colorado School of Mines), V. Shenoy (Brown). Our group is part of a new DOE-BES Computational Materials Science Network (CMSN) project on surface-based nanostructures.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Ho is a Fellow of the APS.

Our Tight Binding MD has been previously recognized as a DOE outstanding scientific accomplishment.

Personnel Commitments for FY2002 to Nearest +/- 10%:

C. Z. Wang (10%), K. M. Ho (5%), visiting scientists: Wencai Lu (30%), students: Hua Wang (60%), Tzu-Liang Chan (100%), Ning Lu (10%).

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$134k

FY04 BA \$150k

FY05 BA \$90k

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics - Theory
Superconductivity Theory

FWP Number: AL-90-540-003

Program Scope:

The objective of this program is to develop theoretical understanding of the properties of superconductors in magnetic fields. We have studied the critical fields, critical currents, ac losses, and the structure and dynamics of vortices and vortex lattices. We have focused much of our attention on the effects of strong anisotropy in the high-temperature cuprate superconductors and of two-gap behavior in MgB_2 .

Major Program Achievements (over duration of support):

- * Introduced concepts of weak-link behavior in granular high-temperature superconductors.
- * Developed theory of two-dimensional pancake vortices and interlayer Josephson vortices in layered high-temperature superconductors.
- * Developed theory for the combined effects of geometrical barriers and bulk pinning on the field-dependent critical current in type-II superconducting strips.
- * Wrote editorials for the *High- T_c Update* newsletter and web site.
- * Using nonlocal London equations, developed theory for vortex-lattice transitions in borocarbides.
- * Using a two-gap model, developed theories predicting different temperature-dependent anisotropies for the upper critical field and the London penetration depth in MgB_2 .
- * Developed a theory for the field dependence of the vortex-core size.

Program impact:

- * New low-noise 77 K SQUIDS are currently being fabricated worldwide following our theoretical predictions that, in the earth's magnetic field, vortices are not trapped in superconducting lines of width less than $\sim 5 \text{ nm}$.
- * The *High- T_c Update* had a major impact on the development of high-temperature superconductivity.
- * Small-angle neutron scattering, scanning tunneling microscopy, and decoration experiments in superconducting borocarbides have confirmed our predictions of vortex-lattice transitions.
- * Different temperature behaviors of anisotropies of the upper critical field and of the penetration depth of MgB_2 have been confirmed in a number of experiments.

Interactions:

- * Internal: P. C. Canfield, D. K. Finnemore, R. Prozorov, and J. Schmalian
- * External: Brookhaven National Laboratory, ETH Zurich (Switzerland), IBM, Institute of Solid State Physics (Moscow, Russia), Los Alamos National Laboratory, Max Planck Institute (Germany), National Institute of Advanced Industrial Science and Technology (Japan), and these universities: Isfahan (Iran), Kansas, Kent State, Napoli (Italy), Notre Dame, Stanford, Tel Aviv (Israel), Texas A&M, Tübingen (Germany), Wisconsin

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

- * VGK and JRC are Fellows of the American Physical Society.
- * also JRC: DOE Annual Award for Sustained Outstanding Research in Solid State Physics, fellow the Institute of Physics, London, founding editor of AIP and APS's *Virtual Journal of Applications of Superconductivity*, editorial boards of *Physical Review B* and *Superconductor Science and Technology*.

Personnel Commitments for FY2005 to Nearest +/- 10%:

J. R. Clem (25%), V. G. Kogan (100%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$247k

FY04 BA \$256k

FY05 BA \$260k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics - Theory

Strongly Correlated Systems

FWP Number: AL-90-540-003

Program Scope:

The development and application of modern approaches in many body theory to novel materials including hard condensed matter systems like unconventional magnets, transition metal oxides, organic conductors, heavy fermion systems, and nearly magnetic systems as well as soft condensed matter systems like micro-emulsions and physical gels formed of block-copolymers. Emphasis is given to the prediction or description of new physical effects and extreme materials properties caused by strong quantum fluctuations, the competition between interactions and disorder as well as between interactions on different length scales. Energy landscape approaches, concepts of field theory and quantum criticality and computational techniques are used.

Major Program Achievements (over duration of support):

1) Theoretical prediction for a new universality class in diluted quantum magnets, including exact determination of the critical exponents at a quantum percolation transition, in all spatial dimensions. Applications include, in addition to disordered magnets, the superconductor-metal quantum phase transition in nanowires and Josephson junction arrays and the Bose-Einstein condensation in atom traps with variable atom concentration. 2) Theory for superconductivity and normal state transport due to strong quantum valence fluctuations in TI-doped PbTe. 3) Developed an analytic theory for strong coupling superconductivity close to quantum phase transitions. Our theory, with direct applications to the ferromagnetic transition in systems with Ising symmetry predicts a large regime with strong order parameter fluctuations in the limit of very strong boson-electron interaction 4) Developed a new theory for the shape variations of cooperatively rearranging regions in super-cooled liquids in excellent agreement with a large class of experiments in organic glass-forming materials 5) Developed a theory for random di-block copolymers explaining the self assembly of block-copolymers in case one of the segments undergoes a glass transition. 6) Development of a new theory for spin liquid behavior in organic superconductors. These computational calculations (using Quantum Monte Carlo techniques) demonstrate that systems with unconventional magnetic ground states and strong magnetic frustration form new superconducting states once made metallic (either by applying pressure or changing chemical composition). This theory explains several puzzling experiments in quasi two-dimensional organic conductors.

Program impact:

Our prediction for a new universality class with in disordered quantum magnets inspired numerous NMR and neutron scattering experiments. Our demonstration of a new self-generated electronic glass state in a correlated material led to several international workshops on complexity and correlations in glasses during the last year. Our theory for pairing in organic conductors motivated and influenced a large number of experimental efforts with very strong evidence for unconventional superconductivity. Our theory for charge Kondo superconductivity, done in close collaboration with an experimental group at Stanford, initiated a number of new experiments. Our prediction for shapes of cooperatively rearranging regions in glass-forming liquids attracted experimental as well as theoretical interest as it allows for a unified view of seemingly contradictory observations.

Interactions:

Internal- CMP (Tringides, Canfield, Johnston, Kogan), Chem. (Mallapragada, Song). External- LANL (Pines, Bishop, Saxena, Curro); ANL (Norman); UCSD (Wolynes), Columbia Univ. (Millis); Univ. of Wisc. (Chubukov), UIUC (Goldbart), UI-Chicago (Morr), Rutgers (Kotliar, Coleman), Univ. of Missouri(Vojta), Ohio State (Trivedi).

Recognitions, Honors and Awards (at least partly due to support under this FWP or subtask):

Early Achievement in Research Award , ISU-Foundation (2003). Research Innovation Award of the Research Corporation (2001). 32 invited talks at major international conferences.

Personnel Commitments for FY2005 to Nearest +/- 10%:

J. Schmalian (PI-30%), M. Dzero (postdoc, 100%), Jun Liu (student-50%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$110k

FY04 BA \$140k

FY05 BA \$145k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory
Magnetic and Electronic Properties

FWP Number: AL-90-540-003

Program Scope: This subtask is the skunkworks for condensed matter theory. It supports projects that are not restricted by specific roadmaps, and as such it has had wonderful success in spawning new initiatives such as a) Phononic Band Gap Materials, b) Magneto-Optics, which quickly evolved to Correlated States, c) Spin Dynamics, d) Mesoscale Ordering, and e) Magnetic Molecules. It was the nurturing place for the Computational Materials Science Network, and has led to funding from the Army for quantum computing simulations. Currently the subtask supports work in molecular dynamics (from first principles, to tight-binding, to classical). It supports work in disordered systems, and it supports work in bridging length scales in magnetism.

Major Program Achievements (recent):

We have developed a method to extract environment-dependent minimal-basis-set orbitals from ab initio wavefunctions. These orbitals give an exact description of the occupied electronic states and are highly localized on the individual atoms. We are using this scheme to develop a new generation of accurate tight-binding (TB) potentials for application to compounds and alloys. We have used TBMD to obtain pathways and barriers for defects in graphene layers. We found a new stable (lower energy) structure for the divacancy cluster.

We have developed a dynamical approach for understanding the properties of random lasers, especially above the laser threshold (*PRL*). When the optical gain is inhomogeneously broadened, we have recently discovered the possibility that some lasing modes are coupled through photon hopping or electron absorption and reemission, which can lead to synchronization of their lasing action for weak coupling, and to antiphase mode locking for strong coupling.

A new mean field theory for treating a central spin decohering in a bath of spins (electron in a quantum dot) has been developed to account for correlation (coherence) effects. We have developed a systematic scheme for dynamical multiscale modeling using statistical coarse graining. It allows the short wavelength modes, which are essential for thermal equilibrium, to be incorporated in models at all length scales. Successful tests of 1D and 2D systems are complete and 3D tests await a new student.

Program Impact:

Our tight-binding potentials have been adopted by many research groups worldwide for molecular dynamics simulations of various complex systems. The light localization and random laser work has attracted attention of several outside groups and collaborations with several research groups are exploiting the theory for new experiments and possible device designs. The multiscale modeling work is being incorporated into a micromagnetics code developed under the Computational Materials Sciences Network.

Interactions:

Internal- Ames Lab Chemistry (K. Ruedenberg, M. Gordon, M. Schmidt)

External - J. R. Chelikowsky (Minnesota); Seoul National University (Korea): Gun-Do Lee; Mingsheng Tang (China); M. Stocks (ORNL); M. Katsnelson (Nijmegen); E. Economou (Greece)

Recognition:

The TB work was awarded the Materials Science Award for Sustained Outstanding Research in Solid State Physics (before this funding period). Ho, Soukoulis, and Harmon are APS Fellows. (As mentioned in the “scope” above, this subtask is vital for exploratory work, and has been remarkably successful.)

Personnel:

C. Z. Wang (70%), K. M. Ho(5%), C. Soukoulis (5%), B. Harmon (5%), Three students (80%).

Authorized Budget (BA) for FY03: \$220k **FY04 BA** \$311k, **FY05 BA** \$230k

Laboratory Name: Ames Laboratory

B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory.
Spin Dynamics

FWP Number: AL-90-540-003

Program Scope: Create, develop, and use first principles methods that will allow accurate simulations at the atomistic level of complex realistic magnetic materials. We partner with ORNL scientists in implementing these methods on modern supercomputers to allow treatment of large unit cells so that thermal and other dynamical properties can be simulated. Exact quantum treatment of spin dynamics for relevant model systems is pursued.

Major Program Achievements (over last 3 years):

Achieved the first consistent explanation of the nature of hysteretic phenomena in the CoPt family of magnets. A practical synergistic combination of first principles, micromagnetic and microstructural simulations was used. We developed an approach for self-consistent calculations of the many body Green function in transition metals and insulators, and used it for ab-initio studies of 3d-, 4d- and 5d- metallic systems. A new general technique for the calculation of exchange coupling parameters and spin waves was developed and used for the study of numerous magnetic systems. Based on spin dynamics simulations, we predicted the existence of large magnetic short range order in itinerant magnets above their Curie temperature. This has the potential to radically change the common view of finite temperature magnetism and could impact many interpretations of experiments related to itinerant magnets. A new classification of magnetic materials based on this short range order idea was proposed. Simulation methods were developed to follow quantum spin oscillations in quantum dots and in magnetic molecules when those systems (qubits) are subjected to decoherence effects caused by a dynamical thermal spin bath of surrounding nuclear spins. An unexpected suppression of decoherence was found and explained for even numbers of qubits. Chaotic spin baths were found to be particularly effective for destroying coherence in qubit systems.

Program Impact:

Our development of first principles spin dynamics (and our treatment of non-collinear magnetism in general) has been widely disseminated, although for large systems the simulation of the thermal fluctuations in very large unit cells is still very demanding and requires considerable supercomputing resources (ORNL). Our newly proposed technique of calculation of exchange parameters is very general and is being used for both localized and itinerant magnetic systems. Our newly developed GW code is publicly available. Several experimental groups have expressed interest in pursuing our predictions of short range magnetic order at high temperatures. The studies on spin bath decoherence are being picked up by NMR experimentalists (at Yale) to analyze recent investigations.

Interactions:

Internal: Ames Laboratory B.McCallum (MEP), R. McQueeney, and F. Borsa (CMP).

External: M. van Schilfgaarde (Arizona State), M. Stocks (ORNL), N. Zein (Russia), M. Auslander (Israel), M. Katsnelson (Nijmegen, the Netherlands), H. De Raedt (Groningen, the Netherlands).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

This project is one of the DOE Science 100 accomplishments (for the first 25 years of DOE). Harmon is a Fellow of American Physical Society and has helped organize focused sessions at three March meetings and the invited symposium at the MMM conference. Both Harmon and Antropov have been on the program committee of the MMM conference. 2 invited review articles, 15 invited talks in last 3 years.

Personnel Commitments for FY2003 to Nearest +/-10%:

V.Antropov (PI-70%), B.Harmon (PI-5%), V. Dobrovitski (40%), Graduate student (50%), postdoc (100%).

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$450

FY04 BA \$421k

FY05 BA \$447k

(Note: Approximately \$140k/year is sent to ORNL(Stocks) as a reconciling transfer for work on this project)

Laboratory Name: Ames Laboratory
B&R Code: KC-02-02-03

FWP and possible subtask under FWP: Condensed Matter Physics, Theory
Left-Handed Materials

FWP Number: AL-90-540-003

Program Scope:

Left-handed materials (LHMs) are composite materials with novel and unique electromagnetic (EM) properties, which are not determined by the fundamental physical properties of their constituents but by the shape and the distribution of specific patterned inclusions. The scope of the program is the theoretical understanding, analysis, development and testing of LHMs, and also the investigation of their feasibility for potential applications.

Major Program Achievements (over duration of support):

Developed a new periodic effective medium description (*PRB 71, 245105 (2005)*) of composite metamaterials, such as LHMs. This new method is able to distinguish the resonant behavior of EM parameters from effects of the periodicity. Our method identifies the origin of the previously observed negative imaginary parts in ϵ and μ , and suggests ways in eliminating all the spurious features that the homogeneous effective medium produces.

Another part of our research concerns the attempts to move the artificial magnetic response and the LH behavior from the microwaves (as in our initial experiments) to the infrared regime. We succeeded to fabricate and to demonstrate the magnetic response of Split Ring Resonator (SRR) structures operating at 6 THz (with FORTH *Opt. Lett. 30, 1348 (2005)*) and, in collaboration the University of Karlsruhe, at 100 THz (*Science 306, 1351 (2004)*) and at 200 THz (*PRL 95, 203901 (2005)*).

We found that the SRRs have a strong electric response, equivalent to that of cut wires, which dominates the behavior of LHMs (*PRL 93, 107402 (2004)*). A criterion was introduced to identify if an experimental transmission peak is left or right handed. If by the closing of the gaps of the SRR, the peak in the transmission, T , vanishes then the material is left-handed. This criterion has been verified experimentally, and it's very useful in designing and fabricating new LHMs.

Program impact:

Provided the first transfer matrix and FDTD calculations of LHMs. Provided the first retrieval procedure to obtain the effective ϵ and μ of LHMs. Our work plays a major role in leading the development of LHMs.

Interactions:

External - E. Ozbay, Bilkent University, Turkey; D. R. Smith, Duke; Boeing's Phantom Works, Seattle; Research Center of Crete, FORTH; M. Wegener, Karlsruhe and J. Pendry, Imperial College.

Recognitions, Honors and Awards (at least partly attributable to support under this subtask):

Soukoulis: Distinguished Professor of Liberal Arts and Sciences, Iowa State University, 2005; Fellow of APS, AAAS and OSA; Senior Alexander von Humboldt Award, 2002.

Invited Talks: Latsis Symposium on *Negative Refraction*, Lausanne, Switzerland, February 2005; *March Meeting of the German Physical Society*, Berlin, March 2005; *PECS-VI (Director)*, Crete, Greece, June 2005. CMS gave also 7 additional invited talks at conferences and 3 seminars at Universities in 2005.

Personnel Commitments for FY2005 to nearest +/- 10%:

Soukoulis (15%), Postdoc: R. Moussa (50%), T. Koschny (40%). Visiting Sci.: E. N. Economou(10%), Peter Markos (20%); 2.5 students(100%); Unpaid associates: E. Ozbay, Jiangfeng Zhou, G. Tuttle.

Authorized Budget (BA) for FY03, FY04, FY05: (New program, in FY03)

FY03 BA\$144k

FY04 BA \$145k

FY05 BA \$197k

FWP and/or subtask title under FWP:

Solidification Science

FWP Number:

AL-90-501-002

Program Scope:

This research area has the overall objective of understanding the dynamic processes of morphological evolution during solid-liquid phase transformations in terms of the fundamental thermodynamic and kinetic properties of the crystal-melt interface and its local response to thermal, solutal, and structural fluctuations. Efforts involve experimental and theoretical investigation of crystal-melt interfaces under equilibrium, near equilibrium and far from equilibrium conditions.

Thermodynamic and kinetic properties that ultimately govern the dynamics of morphological transitions are investigated over all relevant length and time scales with the goal of fundamental theoretical advancement and the development of predictive capability.

Major Program Achievements (over duration of support):

- Experimental quantification of the three-dimensional crystal-melt equilibrium (Wulff) shape for the binary Al-Sn system, expressing the interfacial energy and stiffness in terms of the relevant cubic harmonics.
- Identification of detained mechanistic selection phenomena governing the growth of a twinned bicrystalline faceted dendritic array in hypereutectic Al-Si alloys.
- Establishment of a theoretical lower velocity limit for stable melt-pool behavior and during free-jet melt-spinning, based on melt-pool oscillation and liquid residence time.
- Establishment of a theoretical upper velocity limit for stable free-jet melt-spinning based on momentum transfer, and volume constraints.
- Theoretical estimate of the crystal-melt interfacial mobility in pure aluminum through atomistic simulation using an embedded-atom model and both mechanical and thermal driving forces.
- Incorporated a two-state model to describe the thermodynamic properties of the undercooled liquid and the associated low temperature phase equilibria and partitionless crystallization limits in the Al-La binary system.
- Experimentally investigated the pattern evolution in a confined space (thin slab and cylindrical shapes) and established the lengthscale variation with the sample geometry by using the phase-field model and Hunt/Lu numerical model.
- Experimentally discovered a geometrical constraint controlling the lamellar/rod transition and developed a lamellar/rod transition model to include this constraint.
- Established a local growth model to elucidate the pattern formation in convective growth conditions.
- Developed the capillary sample solidification technique to access the purely diffusive growth process and experimentally measured the intrinsic solute diffusion coefficient in Al-Cu melts.

Program Impact:

The work done in this area is aimed at the critical unresolved fundamental issues related to selection and dynamical evolution of interface morphology and microstructure during solid-liquid phase transformations. Our emphasis on interfacial properties, growth mechanisms, and selection dynamics all address key issues that are both at the scientific forefront of the field and are also the limiting factors in the prediction and control of solidification microstructures.

Interactions:

- Internal: M.J. Kramer and R.W. McCallum (Magnetism Focus Area), C.Z. Wang, and K.M. Ho (*Correlations and Dynamics in Metallic Liquids and Associated Amorphous and Crystalline Systems*).
- External: Alain Karma (Northeastern University), Prof. J.H. Lee (Changwong National University, Korea), DOE Computational Mat. Science Network, *Impurities at interfaces*, J. Danzig (U. Illinois), M. Plapp (EP-Paris), B. Dhindaw (IIT Kharagpur).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

- R.E. Napolitano and J.R. Morris: Organizers "*Frontiers in Solidification Science*," TMS Annual Meeting, 2005.
- R.K. Trivedi: Champion H. Mathewson Medal, The Materials Society (TMS), 2004.
- R.K. Trivedi: Henry Marion Howe Medal from The ASM International.
- R.K. Trivedi: Member, International Advisory Committee, International Conf. on Solidification Processing, 2001, 2003, 2005.

Personnel Commitments for FY2005 to Nearest +/- 10%:

R.E. Napolitano [Coordinator] (40%), I.E. Anderson (20%), L.S. Chumbley (20%), M.J. Kramer (10%), S. Liu (50%), M.I. Mendelev (10%), R.K. Trivedi (20%)

Authorized Budget (BA) for FY03, FY04, FY2005:

FY03 BA ~\$772 k

FY04 BA ~\$772 k

FY05 BA ~\$1150 k

FWP and possible subtask under FWP:

Mechanical Behavior of Materials and Radiation Effects

FWP Number:

AL-90-501-003

Program Scope:

There are three complementary research efforts in this area that are concerned with understanding structural defect behavior at the atomistic through to the microstructural length scale. The largest effort is entitled “Ductile Rare Earth Intermetallic Compounds”, and it is specifically concerned with gaining a more detailed fundamental understanding of the electronic, physical, mechanical, and chemical factors leading to the extraordinarily high room-temperature ductility (>20% elongation) found in certain B2 (CsCl-type) intermetallic compounds with the formula RM (where R is a rare-earth element, M is a non-rare-earth metal). Partly linked to that effort is “Mechanics and Mechanisms of Deformation and Microstructural Evolution,” which involves the development of two- and three-dimensional dislocation dynamics simulation algorithms that better elucidate the cooperative behavior of a very large number of dislocations and their reactions and interactions with point defects, grain boundaries, and second phases. The third effort is concerned with “Atomistic Studies of Defect Structures and Deformation” in condensed systems, and utilizes *ab initio* total energy calculations and molecular dynamics simulations in combination with anisotropic elastic theory to treat long-range elastic interactions and better understand mechanical properties, such as the anomalously high ductility of RM B2 compounds.

Major Program Achievements (over duration of support):

- Single crystal slip line and TEM g-b=0 analyses revealed that $\langle 111 \rangle$ slip occurs in the ductile DyCu B2 intermetallic; $\langle 111 \rangle$ slip is unusual for B2 compounds with high ordering energies. In addition, DyCu appears to produce a non-equilibrium orthorhombic second phase when deformed. This phase may contribute to the toughening behavior.
- Ab initio calculations show that the ductile B2 compounds have unusually low $\frac{1}{2}\langle 100 \rangle\{011\}$ unstable stacking fault energies, which may facilitate easier dislocation motion in these materials.
- Theoretical analyses based on the dislocation line energies revealed that ordinary dislocations in the rare earth B2 compounds YCu, YZn and YAg are intrinsically different from the common B2 intermetallic alloys, such as NiAl.
- Accurately simulated the role of grain size on strengthening of materials using dislocation dynamics. The structure and properties of amorphous carbon using tight-binding molecular dynamics was also accurately simulated.
- Discovered a double-period glide set dislocation structure for Si screw dislocation based on tight-binding and ab initio calculations.

Program impact:

The studies undertaken within this program lead to important insights into the roles of dislocation line tension, anisotropic elastic properties, strain-induced phase transformations, twinning-assisted slip, and grain boundary dislocation sources on the deformation behavior of polycrystalline solids in general. For instance, gaining a better understanding of the anomalously high ductility of the RM B2 intermetallics will improve our knowledge of the broader issue of room temperature ductility in all intermetallics.

Interactions:

S. Agnew (Univ. Virginia) twinning; A. Bastawros (ISU) nanoindentation; E. George (ORNL) environmental embrittlement; Y. Grin (Max Planck Inst.) electron localization function calculations; J. Kruzic (OSU) fatigue; and P. Nash (Ill. Inst. Tech.) heat and free energies of formation. Some of the work by J. R. Morris is supported through the “Alloy Behavior and Design” project supported by BES through ORNL. J. Li (OSU) and S. Yip (MIT) calculations and modeling of dislocation structures; G. Kopidakis and P. C. Kelires (University of Crete, Greece) amorphous carbon; Gun-Do Lee (Seoul National University, South Korea) diffusion and coalescence of vacancy defects in graphene. D. Wolf (ANL) simulating grain growth and grain-boundary sliding during creep and superplastic deformation at the mesoscopic level.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

S.B. Biner –Served as Conference Chair of international conference on “*Micromechanics and Microstructure Evolution: Modeling, Simulation and Experiments*” Sept. 12-16, Madrid, Spain.

K.A. Gschneidner – invited to present talks on ductile RM intermetallics at Fall 2004 MRS meeting and a seminar at the Max-Planck Institute for Chemical Physics of Solids, Dresden, Germany.

Principal Investigator Commitments for FY2005 to Nearest +/- 10%:

S.B. Biner (70%), K.A. Gschneidner, Jr. (10%), T.A. Lograsso (10%), C.H.C. Lo (10%), J.R. Morris, Oak Ridge National Laboratory (10%), A.M. Russell (10%), C.Z. Wang (20%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$276 k

FY04 BA \$526 k

FY05 BA \$505 k

FWP and/or subtask Title under FWP:

Magnetism

FWP Number:

AL-90-501-004

Program Scope:

Research is focused on understanding the interplay between competing energy contributions in determining critical magnetic phenomena in order to formulate and validate a consistent predictive theory describing, and therefore enabling the control of magnetic phenomena at various length scales. Of particular interest are materials systems containing magnetic rare earths, transition metals, or both, where characteristic structural dimensions are on the order of the magnetic interaction lengths, or the energy difference between crystalline states is of the same order as the energy difference between magnetic states. One type of model system is a series of compounds where each member contains a well-defined structural unit of magnetic atoms while the number of atoms in this unit, and/or the arrangement of structural units varies systematically within the series. Because of periodicity, the exchange interactions between rare-earth ions in the units as well as the interactions between the units are well-defined. A second type of model system involves the controlled introduction of either growth or deformation defects into single crystals, while a third approach relies on the self-assembly of nanolayers during the eutectoid decomposition of a single crystal. In all cases, the goal is to understand and manipulate physical interactions propagating over spatial scales from atomistic to macroscopic and temporal scales that vary over several orders of magnitude.

Major Program Achievements (over duration of support):

$\text{Pr}_{(n+1)(n+2)}\text{Ni}_{n(n-1)+2}\text{Si}_{n(n+1)}$, where $n = 2, 3$, and 4 , forms a homologous series of hexagonal compounds whose basic structural unit is a trigonal prism of Pr atoms parallel to the c -axis. The cross-section of the prism is a triangle with 3, 4, and 5 atoms on a side and 0, 1, and 3, interior atoms as n increases. Extensive phase diagram work allowed the preparation of high quality single phase polycrystalline samples and single crystals of these phases. Crystal structures, accurate stoichiometries, magnetic, and thermodynamic properties have been determined for all three compounds in the series. Thermal expansion and magnetostriction measurements on polycrystalline samples were completed for $n=3$ and 4 and preliminary neutron diffraction measurements have been performed on the $n=3$ compound. Between 100 and 400 K, the paramagnetic dc susceptibility, χ parallel and perpendicular to the c -axis is reasonably approximated by a Curie-Weiss law for all three compounds. The paramagnetic moment, is close to the free-ion moment for Pr^{3+} . In all cases, the Weiss temperature, θ , is higher for $H\parallel c$ than for $H\perp c$. For $H\parallel c$, θ_{\parallel} increases with increasing n (the size of the prismatic columnn), while for $H\perp c$, θ_{\perp} decreases with increasing n . All three compounds order magnetically below 100K. For $H\parallel c$ the compounds exhibit ferromagnetic ordering temperatures which are in good agreement with the corresponding θ_{\parallel} values. For $H\perp c$, a peak in the low-field M vs T plots appears at temperature corresponding to the values of θ_{\perp} . For the three compounds at 5 K, the magnetization as a function of applied field for $H\parallel c$, saturates rapidly and is weakly field dependent, as typical for ferromagnets. The saturation magnetization depends strongly on n . The observed values are between 25 and 50%, of the theoretical value of $gJ = 3.2 \mu_B/\text{Pr}$. For $H\perp c$, for all three compounds, when $H < 2\text{T}$, dM/dH is small. Between 2 T and 3 T, for all three compounds, a metamagnetic transition is observed, while for $H > 3\text{T}$ dM/dH is also small. Based on the systematics of the properties of the members of the series, a model for site-specific interactions has been developed for comparison with first principles calculations. Preliminary studies of GdMg , GdAg , and Tb-Mg indicate a dependence of M_s on defect density, a ferromagnetic antiphase boundary in an antiferromagnet, and interacting nanolayers, respectively.

Program Impact:

By exploiting the availability of distinct structural units varying in size from a fraction of a nanometer to several nanometers and their self-assembly of crystallographic grains ranging from a few nanometers to centimeters in size, the fundamental relationship between magnetic and structural landscapes in determining the magnetic properties of complex materials will be clarified. The ability to produce extremely high purity single crystal samples allows direct comparison with first principles calculations.

Interactions:

Internal—P. C. Canfield and B. N. Harmon (Condensed Matter Physics); G.J. Miller (Chemistry).

External—Anna Llobet Megias, LANL; Argonne and Brookhaven National Labs; Iowa State University.

Personnel Commitments for FY2005 to Nearest +/- 10%:

R.W. McCallum [Coordinator] (60%), K.A. Gschneidner, Jr. (30%), D.C. Jiles (10%), T.A. Lograsso (10%), V.K. Pecharsky (30%), J.E. Snyder (40%)

Authorized Budget (BA) for FY03, FY04, FY2005:

FY03 BA ~\$1163 k

FY04 BA ~\$1256 k

FY05 BA ~\$1060 k

FWP and possible subtask under FWP:

Extraordinary Responsive Magnetic Rare Earth Materials

FWP Number:

AL-90-501-004

Program Scope:

Coordinated experimental and theoretical investigations of the magnetic-displacive phase transformations in R_5T_4 alloys, where R is rare earth metal and T is main group IV element – Si, Ge, Sn – or mixtures thereof, plus small substitutions of the tetravalent elements by trivalent Ga or pentavalent Sb. The research is focused first, on the understanding of the underlying electronic structure, the microscopic and macroscopic interactions that bring about extremely strong coupling of the magnetic moments with the lattices and second, on developing and validating models of the magnetic-displacive transformation in order to facilitate future design of novel material systems exhibiting extremely large responses to small changes of magnetic field, temperature and pressure.

Major Program Achievements (over duration of support):

- Established protocols for the preparation of R_5T_4 single crystals by both Bridgman and Czochralski techniques.
- Discovered that exchange interactions and single ion-anisotropy play a major role in the stability of the R_5T_4 phases.
- Developed X-ray powder diffraction with *in situ* low temperature and high magnetic field capabilities to map the field-induced structural transformations in R_5T_4 compounds, thus linking crystallographic and physical property data.
- Discovered that the displacive, structural-only transformation in Er_5Si_4 can be affected by magnetic fields of 50 kOe or higher with the compound in the true paramagnetic state, i.e., ~ 200 K above its magnetic ordering temperature.
- Discovered that low-temperature, high-magnetic field, high-pressure, and high-silicon content phases near the $Gd_5Si_2Ge_2$ stoichiometry are structurally indistinguishable, thus these four different thermodynamic variables have a similar effect on the magnetic-displacive transformations in the R_5T_4 family.
- Established that the largest magnetocaloric effect is observed when a material orders magnetically *via* a first-order coupled magneto-structural transformation.
- Quantified the lattice contribution to the giant magnetocaloric effect.
- Discovered and mapped out regions where R_5T_4 compounds exist in phase separated states.
- Demonstrated that a structural change results in anisotropic magnetoresistance of $Gd_5Si_2Ge_2$ due to a significant reduction of electronic velocity in the [100] direction and the anisotropy of the electrical conductivity.
- Employed exchange coupling calculations to obtain the effective Heisenberg model parameters of $Gd_5Si_2Ge_2$.
- Computed the free energy of $Gd_5Si_2Ge_2$ as a function of temperature using the mean-field approximation, reproduced a first order magneto-structural phase transition with a large value of $|\partial M/\partial T|$ which is observed experimentally.

Program Impact:

This research is being carried out by a multi-disciplinary team of researchers from the Materials and Engineering Physics, Condensed Matter Physics and Materials Chemistry Programs. A number of experimental and theoretical approaches have been brought to bear on these extraordinary R_5T_4 materials in order to understand their nature.

Interactions:

Efforts on the basic studies of magnetic-displacive phase transformations are carried out in collaboration with scientists at the US DOE Brookhaven and Argonne National Laboratories; UCLA; University of Amsterdam, the Netherlands; University of Modena, Italy; Istituto Elettrotecnico Nazionale Galileo Ferraris, Turin, Italy; University of Campinas and Rio de Janeiro, Brazil; University of Saragosa, Spain; Centre for Advanced Technology, Indore, India; Imperial College, London, UK; and Institute of Physics of Czech Academy of Sciences, Prague, Czech Republic.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

K.A. Gschneidner, Jr. – Honorary Member of the Japan Institute of Metals (2001), Fellow of the American Physical Society (2002); D.C. Jiles – Distinguished Professor, Iowa State University (2003); V.K. Pecharsky – Editor of *Handbook on the Physics and Chemistry of Rare Earths* (2001), Materials Science and Engineering Department Excellence in Research Award (2003). V.K. Pecharsky – organizer of relevant sessions at international conferences (ICFE, Geneva, 2003; 20th CMD EPS, Prague, 2004, 24th Rare Earth Research Conference, Keystone, CO, 2005). Over 45 plenary, keynote and invited talks 2000-2005.

Personnel Commitments for FY2005 to Nearest +/- 10%:

K.A. Gschneidner, Jr. [Co-coordinator] (30%), V.K. Pecharsky [Co-coordinator] (30%), L.S. Chumbley (10%), D.C. Jiles (10%), T.A. Lograsso (10%), G.J. Miller (10%), J.E. Snyder (20%)

Authorized Budget (BA) for FY03, FY04, FY2005:

FY03 BA ~\$820 k

FY04 BA ~\$902 k

FY05 BA ~\$1011 k

FWP and possible subtask under FWP:

Science of Amorphous and Aperiodic Materials

FWP Number:

AL-90-501-006

Program Scope:

The primary scientific goals in this effort are directed towards gaining an increased fundamental understanding of (i) the correlation between short-range atomic order and the devitrification and deformation behavior in amorphous systems and (ii) the role of crystal chemistry (*i.e.*, composition, bonding and coordination) in controlling the structural stability of aperiodic systems. Amorphous and aperiodic structures, while nearly opposite in terms of long-range atomic order have significant interrelationships, particularly in regard to their short-range atomic order. Research efforts within this program include synthesis, structure determination and theoretical modeling studies that seek to couple pair correlation analyses with liquid and solid systems.

Major Program Achievements (over duration of support):

- Obtained direct validation of *ab initio* calculations that predicted a metastable state within a narrow Zr-(Pd,Cu) composition range using high-energy X-ray diffraction
- Discovered that phase selection in Zr-Pt alloys during solidification from the liquid and devitrification from an amorphous phase changes from stable to metastable with < 1 at% change in composition.
- Synthesized single grains of quasicrystalline and approximant Cd-Yb phases and determined their common atomic clusters using both high-resolution TEM and high-energy X-ray diffraction.
- Coupled fully atomistic MD with quasi-continuum FEM simulations to illustrate that a pressure dependent yield surface, contrary to crystalline solids, develops in metallic glasses due to free volume evolution and produces a tension-compression asymmetry.
- Performed MD simulations that, in agreement to experimental creep studies, show free volume is the principal mechanism responsible for homogeneous deformation behavior of metallic glasses. Moreover, high-energy X-ray diffraction data obtained from orthogonal directions revealed that free volume created during creep is anisotropic (*i.e.*, average bond distances are larger along the loading axis than perpendicular to this direction).

Program impact:

This effort provides critical insights into the intricate dynamics and transformation conditions affecting glass formation, non-equilibrium phase selection during devitrification, and formation of stable aperiodic and related approximant structures. Advanced high-energy X-ray scattering analysis techniques are leading to new descriptions of anisotropic free volume evolution during homogeneous deformation of metallic glasses. Collectively, these insights are also enabling the development of predictive capabilities using computational and theoretical approaches.

Interactions:

- Materials Chemistry and Condensed Matter Physics Programs at the Ames Laboratory to study surfaces and interfaces of quasicrystals as well as solute effects on metastable phase selection from metallic glasses
- Advanced Photon Source at the Argonne National Laboratory to perform dynamic structural investigations with high-energy X-ray scattering in time-resolved and isothermal modes
- Argonne National Laboratory, Materials and Engineering Physics Program to utilize their fluctuation electron microscopy capabilities to study medium-range order in amorphous Zr-Pd and Zr-Pt materials
- Institut Laue-Langevin to perform neutron diffraction of natural and isotopically-enriched liquid $\text{Cd}_{84}\text{Yb}_{16}$

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

M.J. Kramer, T.A. Lograsso and Y. Wu, – MRS Fall 03 Best Poster Award
D.J. Sordet – Chair, MRS Fall 03 Quasicrystal Symposium and 9th International Conference on Quasicrystals
T.A. Lograsso – Organizer, BES Workshop on Design, Discovery and Growth of Novel Materials, 2003
S.B. Biner – Chair, ECI Modeling and Simulation of Micromechanics and Microstructure Evolution 2005
M.J. Kramer – Member of Spallation Neutron Source POW-GEN3 Instrument Advisory Team
55 publications and 28 invited talks since 2003

Principal Investigator Commitments for FY2005 to Nearest +/- 10%:

D.J. Sordet [Coordinator] (20%), S.B. Biner (30%), M.J. Kramer (50%), T.A. Lograsso (10%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$815 k

FY04 BA \$851 k

FY05 BA \$899

FWP and/or subtask title under FWP:

Structure of Liquid Metals

FWP Number:

AL-02-501-044

Program Scope:

The main research goal of this effort is to understand the structure and dynamics of liquid metals and alloys, both in equilibrium and in the supercooled state, in relation to the competition between (and dynamics of) crystal nucleation and glass formation. The effort ranges from accurate *ab initio* simulations of liquids, large-scale simulations of liquids and solid-liquid interfaces. Calculations of phase diagrams, non-equilibrium theory of glass formation, as well as experiments using X-ray and neutron scattering are used to examine and confirm structural and dynamical properties.

Major Program Achievements (over duration of support):

- Temperature variation of the structure and microstructure of molten eutectic $Al_{1-x}Si_x$ alloys ($x=0, 0.125$ and 0.18) has been determined by neutron diffraction and small-angle neutron scattering.
- *Ab initio* molecular dynamics simulation have been performed to study the structure of liquid AlCu at the eutectic composition and compared to the results from X-ray scattering.
- An accurate tight-binding potential for Ge has been developed. Tight-binding molecular dynamics has been performed to study liquid Al, Si, and Ge. Tight-binding potentials for Al-Si and Al-Ge liquid alloys are under development.
- A new EAM potential for Al has been developed and molecular dynamics simulations have been performed to study the supercooled Al liquid. Different rapid solidification behavior (i.e., crystallization vs. verification) has been observed from two different EAM Al potentials which exhibit different local order structure in the liquid state.
- Thermodynamic calculations have been performed to determine the T_0 curves for five simple eutectic binary alloys and for Al-rare earth (RE) alloys with intermediate compounds. The results showed that the glass forming composition of the Al-RE alloys is strongly correlated with the partitioning crystallization zone bounded by the T_0 curves, suggesting that restriction of material transport is a key factor governing the formation of glass in these systems.
- Molecular dynamics simulations have been performed to study the liquid-glass transition in a single component system (i.e., Al). The transition is determined to be first order where liquid-glass coexistence is observed for the first time.
- The phase diagram for the liquid-glass transition of a model density functional as function of the virial coefficients of the liquid has been determined by a dynamical mean field theory for self-generated glasses.

Program Impact:

The competition between crystal nucleation and glass formability depends on the structure, dynamics, and thermodynamic stability of a liquid alloy, yet little effort has been spent on detailed studies of these properties at the smallest length scales. The difficulty in predicting even equilibrium properties (such as phase diagrams) makes the understanding of non-equilibrium properties such as glass formability an important challenge.

Interactions:

- Contribution to theoretical efforts within scope of the Computational Materials Science Network (US DOE) project, "Fundamentals of dirty interface: from Atoms to alloy microstructures"
- *In-situ* diffraction studies at the Advanced Photon Source (Argonne National Laboratory) MU-CAT beamline.
- Large-scale computations at the National Energy Research Scientific Computing Center (NERSC)
- CNRS Laboratoire de Science et Génie des Matériaux et de Métallurgie at the Ecole des Mines de Nancy to analyse the structure of liquid and amorphous metallic alloys using neutron scattering techniques

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

- J.R. Morris and R.E. Naplitano: Organizer "*Frontiers in Solidification Science*" TMS Annual Meeting, 2005.
- J. Schmalian: Organizer Aspen Center for Physics workshop on *Dynamics and Correlations in Glasses*, 2005; Organizer, Institute for Theoretical Physics (UCSB) Miniworkshop on *complexity in correlated materials*, 2005; Member, Science Steering Committee, Institute for Complex Adaptive Matter, Univ. of California (2004-2005).
- D.J. Sordélet: Co-organizer, *9th International Conference on Quasicrystals (ICQ9)*, 2005; Member of International Program Committee for *12th International Conference on Liquid and Amorphous Metals (LAM12)*, 2004; Member of the International Advisory Board for *International Conference on Solidification Science and Processing (ICSSP)*, 2004.

Personnel Commitments for FY2005 to Nearest +/- 10%:

M.J. Kramer (10%), M.I. Mendelev (50%), J. Schmalian (10%), X. Song (10%), D.J. Sordélet (10%), C.Z. Wang (10%)

Authorized Budget (BA) for FY03, FY04, FY2005:

FY03 BA ~\$400 k (first full year of funding)

FY04 BA ~\$415 k

FY05 BA ~\$380 k

FWP and possible subtask under FWP:
Materials Preparation Center

FWP Number:
AL-96-501-006

Program Scope:

The Materials Preparation Center (MPC) is a provider of exceptionally high quality research scale quantities of specialized materials and services to academic, national laboratory and industrial requesters worldwide. The unique materials synthesis and processing capabilities, which have been largely developed with Department of Energy (DOE) support of this national Specialized Single-Purpose User Facility, are made available on a cost recovery fee basis. The MPC thus enables fundamental research and development of materials-dependent technologies by providing commercially unavailable materials and processing services. Key capabilities of the MPC include the synthesis and crystal growth of complex alloys, the processing of high-purity rare earth metals and alloys, and the synthesis of high purity metallic powders. Importantly, the MPC critically supports the Basic Energy Science (BES)-sponsored research projects within the Materials and Engineering Physics (MEP) Program at the Ames Laboratory. The MPC also performs processing-related research via the "Process Science Initiative" (PSI). The PSI provides support for synthesis and processing research that contributes directly to BES-sponsored projects within the Ames Laboratory. Such targeted synthesis and processing science efforts specific to the MEP Program's research portfolio enable greater progress in and breadth to the experimental, materials-dependent research being conducted.

Major Program Achievements (over duration of support):

- Synthesized La-Ni-Sn cryocooler alloy for the ESA/NASA Plank mission vehicle. The hydrogen storage bed materials will be used for the space-based observation vehicle, scheduled for launch in 2008.
- Established benchmarks for Al-Y-Ni-Co alloy powder purity and performance for DARPA's Structural Amorphous Materials (SAM) Program.
- Establishment of theoretical lower and upper velocity limits for stable melt-pool behavior during free-jet melt-spinning.
- Determined the phase reaction sequence in actively-reinforced composites during consolidation processing by time-resolved in situ neutron diffraction that permits design of the processing method to control residual stress state, enabling study of its influence on composite strengthening using SMARTS system.
- Enhanced alloy phase space determination through a combination of thermodynamic modeling and experimental methods, which led directly to significant improvements in the synthesis of single crystal Pr-Ni-Si compounds.
- Developed a low-cost carbothermic reduction process for synthesis of intermetallic rare earth compounds, R_5X_4 , where R is a rare earth metal and X are metals of Group 11A or IVA or mixtures thereof.
- Developed a low cost synthesis process for the formation of a TaC layer for the inner surface of tantalum crucibles to serve as a barrier to contamination of the rare earth intermetallic alloys.

Program impact:

The MPC is a source and developer of unique capabilities in the preparation, purification, processing and synthesis of metals and alloys for advanced energy and technology research. In particular, the MPC enables scientific excellence by preparing research samples of significant quality and size. There is a great deal of science associated with this, to the extent that the continual need for unique material samples is, itself, one of the science drivers for the MPC. In addition, the MPC is involved via the PSI in basic science efforts directed toward the preparation of materials that are specifically germane to BES-supported projects. The MPC staff also contribute to the scientific training of students and postdoctoral researchers in the areas of materials processing and synthesis. All MPC work is non-competitive to commercial entities.

Interactions:

- D. Brown (LANL-LANSCE), F. Tang (ORNL), N. Chwala (Arizona State University): Actively-reinforced Composites
- 126 individual researchers requests for materials and services were completed in FY05, generating \$619K.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

T.A. Lograsso – Organizer, BES Workshop on Design, Discovery and Growth of Novel Materials, 2003

Principal Investigator Commitments for FY2005 to Nearest +/- 10%:

L.L. Jones [Director] (50%), T.A. Lograsso [Associate Director] (10%)

Authorized Budget (BA) for FY03, FY04, FY05:

FY03 BA \$831 k

FY04 BA \$831 k

FY05 BA \$802